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ISOLATION AND STRUCTURAL DETERMINATION OF VULGARONE A AND B, TWO NOVEL SESQUITERPENE KETONES FROM *CHRYSANTHEMUM VULGARE*

Y. Uchio
Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, Japan

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Abstract—Two new sesquiterpene ketones, vulgarone A and B, were isolated from the essential oil of *Chrysanthemum vulgare*. The structures were determined based on comparison of the spectral properties with those of chrysanthenone and verbenone, and on the chemical interconversion.

Chrysanthemum vulgare (L.) Bernh. (*Tanacetum vulgare* L.) is a medicinal plant widely distributed in Europe, Siberia and N. America. Although the essential oil of the plant has been investigated by a number of workers,[1–5] the previous reports deal mainly with the monoterpene constituents and hardly with the sesquiterpenes.[6,7] The present author investigated the sesquiterpene constituents of the plant to isolate two novel ketones named vulgarone A and B, whose structures and absolute configurations were determined as β,γ-unsaturated ketone (1) and α,β-unsaturated ketone (2), respectively. Since the IR, ^{1}H NMR and ^{13}C NMR spectra of the two ketones are similar to those of chrysanthenone (5) and verbenone (10), the structural studies have been directed to detailed comparisons of the spectroscopic properties, together with some chemical reactions of these compounds. In addition, vulgarone B (2) was synthesized by allylic methylene oxidation of α-longipinene, and vulgarone A (1) was prepared by photochemical transformation of vulgarone B (2). The present author describes the detailed spectral and chemical evidence for the proposed structures. Parts of this paper have been published in preliminary communications.[8,9]

The essential oil was separated by a combination of fractional distillation and successive column and tlc over silica gel to isolate vulgarone A and B, respectively in yields of 7.6 and 11.9%, together with (−)-chrysanthenone (5) which was a main component (18.9%).

Structure of vulgarone A. Vulgarone A was isolated as an oily substance, $[\alpha]_D^{25} + 113.7°$ (c 0.95, CHCl$_3$). The molecular formula was determined as $C_{15}H_{22}O$ (M^+ 218.1653) in high resolution mass spectrometry, and the IR and ^{1}H NMR spectra revealed the presence of the following functional groups: three tertiary Me's (δ 0.93, 1.01 and 1.18, each 3H, s), a trisubstituted double bond bearing a Me ($\nu_{C=C}$ 3040, 1650 and 830 cm^{-1}; δ 1.78, 3H, t, J = 2.0 Hz and δ 5.58, 1H, m), a CO group ($\nu_{C=O}$ 1780 cm^{-1}), an allylic methine (δ 2.38, 1H, br.s, Wh/2, 7.0 Hz), and two methines adjacent to the CO group (δ 2.62, 1H, dd, J = 7.0 and 1.0 Hz; δ 2.78, 1H, ddd, J = 7.0, 2.5 and 1.5 Hz). The IR absorption of a CO group ($\nu_{C=O}$ 1780 cm^{-1}) indicated the ketone group to be 4-membered one,[10] and the UV spectrum showed a maximum due to $n \rightarrow \pi^*$ transition at 292 nm (ϵ = 88) which is attributable to a β,γ-unsaturated ketone.[11] These values were in agreement with those ($\nu_{C=O}$ 1780 cm^{-1}; λ_{max} 295 nm, ϵ = 144) of chrysanthenone (5). Although vulgarone A contains one more isoprene unit than chrysanthenone, such a close resemblance in the functional groups, suggested that the ketone would contain a partial structure of chrysanthenone (5). The structural similarity between vulgarone A and chrysanthenone was supported by comparison of the ^{13}C NMR spectra of both ketones, which are listed in Table 1 together with that of α-pinene. The C atoms of C-4 and C-10, which were assigned respectively to the methylene and Me carbons in both chrysanthenone (5) and α-pinene, were replaced by methine and methylene carbons in vulgarone A. The remaining carbons of main skeletons showed a good coincidence in the chemical shifts and peak multiplicity between vulgarone A (1) and chrysanthenone (5). This fact indicated that the additional isoprene unit consisting of two methylenes and one gem-dimethyl was to be inserted between C-4 and C-10 in the molecule of chrysanthenone (5). Thus, the gross structure of vulgarone A was depicted by formula 1. This structure was reasonably explained by the characteristic fragment ions of the mass spectrum at *m/e* 190.1744 ($C_{14}H_{22}$, M–CO, 18%), 119.0863 (C_9H_{11}, M–CO–C_5H_{11}, 100%) and 106.0780 (C_8H_{10}, M–CO–C_6H_{12}, 50%), the generation of which is respectively consistent with the elimination of a CO group from the molecular ion and the successive ruptures of the C_4–C_{13} and C_{10}–C_{11}, or the C_4–C_{13} and C_6–C_{10} bonds. It was also supported by the aromatic solvent-induced ^{1}H NMR spectra as shown in Table 2. Furthermore, decoupling experiments supported the proposed structure of the molecule.

When the olefinic proton at δ 5.58 was irradiated, the triplet of the olefinic Me at δ 1.78 was transformed into a doublet (J = 2.0 Hz), the broad singlet of the allylic methine at δ 2.38 into a slightly narrow singlet (Wh/2, 5.5 Hz), and the double doublet at δ 2.62 and the double quartet (ddd) at δ 2.78 of both α-methines to the CO group respectively into a sharp doublet (J = 7.0 Hz) and a double doublet (J = 7.0 and 2.5 Hz); irradiation of the allylic methine proton at δ 2.38 caused the triplet of the olefinic Me at δ 1.78 to change into a doublet (J = 2.0 Hz). In addition, double irradiation of the olefinic Me (1.78) and the middle between the double doublet (2.62) and double quartet (ddd, 2.78) caused the multiplet of the olefinic proton (5.58) to become a doublet (J = 2.5 Hz); double irradiation of the olefinic Me (1.78) and allylic methine (2.38) reformed the multiplet (5.58) into a singlet (Wh/2, 2.0 Hz), and that of the olefinic proton (5.58) and the allylic methine (2.38) reformed the triplet (1.78) into a

Table 1. ^{13}C NMR spectra[a] of vulgarone A (1) and B (2), chrysanthenone (5), 4-oxo-α-ylangene (9), verbenone (10) and α-pinene (11)

compound	1	5	2	9	10	11[b]
C-1	68.6 (d)	67.9 (d) (Δδ+20.7)[c]	50.6 (d)	46.6 (d)	49.6 (d)	47.2 (d)
C-2	139.7 (s)	138.7 (s)	172.4 (s)	169.2 (s)	169.8 (s)	144.4 (s)
C-3	121.4 (d)	118.4 (d)	122.5 (d)	122.1 (d)	121.0 (d)	116.1 (d)
C-4	55.6 (d)	33.0 (t)	204.7 (s)	202.7 (s)	203.2 (s)	31.5 (t)
C-5	65.1 (d)	62.6 (d) (Δδ+21.7)[c]	66.8 (d)	64.1 (d)	57.5 (d)	40.9 (d)
C-6	37.1 (s)	30.1 (s)	55.1 (s)	56.6 (s)	53.7 (s)	38.1 (s)
C-7	205.7 (s)	205.8 (s)	58.0 (d)	56.2 (d)	40.6 (t)	31.3 (t)
C-8	23.5 (q)	23.0 (q)	22.9 (q)	20.3 (q)	21.9 (q)	20.9 (q)
C-9	27.7 (q)	27.3 (q)	24.7 (q)	23.8 (q)	23.4 (q)	22.9 (q)
C-10	33.2 (t)	14.7 (q)	38.6 (t)	36.6 (t)	26.5 (q)	26.5 (q)
C-11	21.5 (t)		21.4 (t)	22.1 (t)		
C-12	42.2 (t)		41.6 (t)	44.9 (d)		
C-13	35.2 (s)		33.8 (s)	31.9 (d)		
C-14	26.1 (q)[d]		27.3 (q)[d]	19.4 (q)[d]		
C-15	30.4 (q)[d]		27.8 (q)[d]	19.6 (q)[d]		

[a] Shifts (δ) in ppm relative to TMS. Multiplicities are given in parentheses by the off-resonance ^1H decoupled spectra. [b] The numbering system follows the same as verbenone (10). [c] $\Delta\delta = \delta C^{ketone} - \delta C^{hydrocarbon}$ in ref. 22. [d] Assignment may be interchanged.

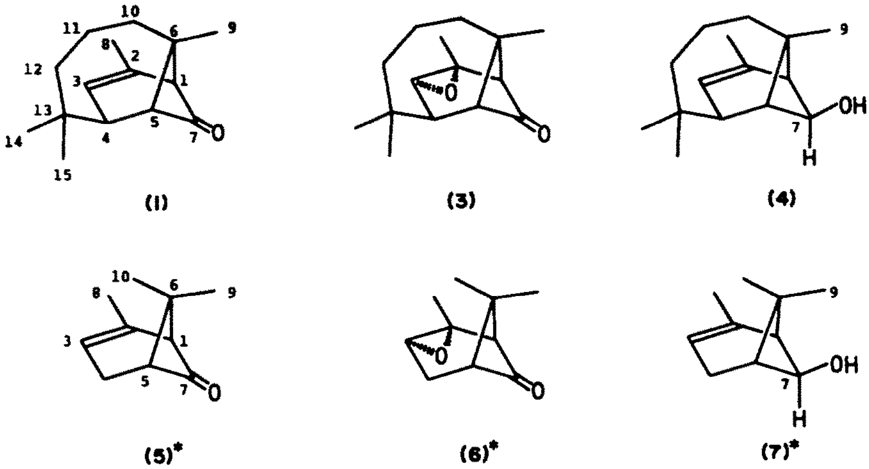
Table 2. ^1H NMR spectra (δ in ppm) of vulgarone A (1) and chrysanthenone (5), and the aromatic solvent-induced shifts

compound		1[a]						5[a]				
		CCl_4	C_6D_6	$\Delta\binom{CCl_4-}{C_6D_6}$	C_6F_6	$\Delta\binom{CCl_4-}{C_6F_6}$[b]		CCl_4	C_6D_6	$\Delta\binom{CCl_4-}{C_6F_6}$	C_6F_6	$\Delta\binom{CCl_4-}{C_6F_6}$[b]
H-1	dd	2.62	2.53	+0.09	2.54	+0.08						
H-3	m	5.58	5.43	+0.15	5.67	-0.09	m	5.30	5.00	+0.30	5.34	-0.04
H-4	br(s)	2.38	2.31	+0.07	2.21	+0.17						
H-5	ddd	2.78	2.78	0.00	2.71	+0.07						
H-8	t	1.78	1.50	+0.28	1.80	-0.02	q	1.70	1.41	+0.29	1.73	-0.03
H-9	s	1.18	1.02	+0.16	1.19	-0.01	s	1.20	1.00	+0.20	1.22	-0.02
H-10 H-11 H-12	m	1.25 ~ 1.65	1.10 ~ 1.40		1.30 ~ 1.70		s	1.18	0.91	+0.27	1.28	-0.10
H-14	s	0.93	0.69	+0.24	0.99	-0.06						
H-15	s	1.01	0.82	+0.19	1.08	-0.07						

[a] Couplings (Hz) of 1: $J_{1,3}=1.0$; $J_{1,5}=7.0$; $J_{3,5}=1.5$; $J_{3,4}=J_{4,5}=2.5$; $J_{3,8}=J_{4,8}=2.0$;
5: $J_{3,8}=J_{4,8}=2.0$.
[b] Cf. ref. 23.

singlet. The decoupling experiments revealed that in the molecule of the ketone cross-ring ($J_{1,5} = 7.0$ Hz),[12] allylic ($J_{1,3} = 1.0$ and $J_{3,8} = 2.0$ Hz), vicinal ($J_{3,4} = J_{4,5} = 2.5$ Hz), homoallylic ($J_{4,8} = 2.0$ Hz) and M arrangement ($J_{3,5} = 1.5$ Hz) couplings are present and H-4 shows no additional couplings to other protons. Such a coupling system has been reported on molecule of verbenone,[13] and *cis*-verbenol[13] which contain the framework of α-pinene as well as chrysanthenone, and this result supports the structure (1) which holds gem-dimethyls on C-13. Additionally, the further support of the structure obtained by preparation of the derivatives, epoxide and alcohol.

Vulgarone A was treated with *m*-chloroperbenzoic



*Structures of (5), (6) and (7) are shown in a series of antipodes in the present work.

Fig. 1.

acid to give only an epoxide (3), $C_{15}H_{22}O_2$, m.p. 105.5–106.5°, and was reduced with LAH to afford only an alcohol (4), $C_{15}H_{24}O$, m.p. 50.5–52.0° (3,5-dinitrobenzoate, m.p. 142.5–143.5°), respectively in quantitative yields as well as the case of chrysanthenone. The ^1H NMR spectra of both derivatives and the solvent effects on chemical shifts of the alcohol (4) closely resemble those of chrysanthenone epoxide (6) and *cis*-chrysanthenol (7). In particular, as seen in Table 3, the signals of the Me group (H-9) and the secondary carbinyl proton (H-7), which are in 1,3-diaxial positions, were almost superimposable with corresponding ones of *cis*-chrysanthenol (7) in both CCl_4 and C_5D_5N. These chemical and spectral data showed that the configuration of the epoxide ring of 3 is the same as chrysanthenone epoxide (6)[14] with respect to the CO group and one of the OH groups of 4 as *cis*-chrysanthenol (7) with respect to the bridgehead Me group. The formation of these derivatives can be reasonably explained by considering that the reactions occurred under the steric hindrance of the bridged methylenes and the Me group on a bridgehead, respectively.

Vulgarone A showed a positive Cotton effect ($[\phi]_{307}$ + 6490, $[\phi]_{291}$0, $[\phi]_{273}$ − 3680, a = 101.7, *c* 0.23 in isooctane) on the ORD curve. This fact indicated that the β,γ-unsaturated CO system is arranged as the same dissymetric chromophore in the molecule as that of (+)-chrysanthenone ($[\phi]_{311}$ + 9000, $[\phi]_{296}$0, $[\phi]_{276}$ − 8030, a = 170.3, *c* 0.18 in isooctane).[15] Accordingly, the absolute configuration of vulgarone A is depicted by stereostructure 1. The final confirmation of this structure was obtained by photochemical transformation of vulgarone B as will be shown later.

Structure of vulgarone B. Vulgarone B (2), m.p. 35.5–36.0°; $[\alpha]_D^{25}$ + 63.4° (*c* 1.10, $CHCl_3$); semicarbazone (m.p.

Table 3. ^1H NMR spectra (δ in ppm) of the alcohol (4) and *cis*-chrysanthenol (7), and the solvent induced-shifts

compound		4^a				7^b		
		CCl_4	C_5D_5N	$\Delta\binom{CCl_4-}{C_5D_5N}$		CCl_4	C_5D_5N	$\Delta\binom{CCl_4-}{C_5D_5N}$
H-1	dd	1.92	2.18	−0.26				
H-3	m	5.42	5.51	−0.09	m	5.13	5.18	−0.05
H-4	m	2.08	2.18	−0.10				
H-5	ddd	2.26	2.52	−0.26				
H-7	s	3.80	4.19	−0.39	s	3.86	4.19	−0.33
H-8	t	1.70	1.69	+0.01	q	1.63	1.61	+0.02
H-9	s	1.50	1.86	−0.36	s	1.52	1.84	−0.32
H-10 } H-11 } H-12 }	m	1.10 ~ 1.70	1.20 ~ 1.80		s	0.88	0.98	−0.10
H-14	s	0.93 {	0.91 {					
H-15	s	0.96	0.96					

[a] Couplings (Hz) of 4: $J_{1,5}=7.0$; $J_{1,3}=1.0$; $J_{3,10}=J_{4,5}=J_{4,10}=2.0$.

Irradiation at 5.42 ⟶ 1.70 (d, J=2.0), 1.92 (d, J=7.0), 2.26 (dd, J=7.0, 2.0)

[b] $\Delta(CDCl_3-C_5D_5N)$: see ref. 24.

Table 4. ^1H NMR spectra (δ in ppm) of vulgarone B (2) and verbenone (10)

compound	2^a			10^b		
		C_6D_6	$\Delta\binom{CCl_4-}{C_6D_6}$		C_6D_6	$\Delta\binom{CCl_4-}{C_6D_6}$
H-1	dd	2.12	+0.34	ddd	1.92	+0.40
H-3	sext	5.74	-0.13	sext	5.66	-0.08
H-5	dd	2.80	-0.17	ddd	2.59	-0.12
H-7	s	2.02	-0.03	d α	1.76	+0.23
				ddd β	2.39	+0.35
H-8	d	1.52	+0.46	d	1.54	+0.46
H-9	s	0.86	+0.10	s	0.86	+0.14
H-10	m	1.10 ~ 1.50		s	1.17	+0.33
H-11						
H-12						
H-14	s	0.71				
H-15	s	0.76				

[a] Couplings (Hz) of 2: $J_{1,5}=6.5$; $J_{1,3}=J_{3,5}=J_{3,8}=1.5$.

[b] The couplings are almost the same as those in ref. 13.

221.0–221.5°), was analyzed to be $C_{15}H_{22}O$ (M^+ 218.1684) in high resolution mass spectrometry and elemental analysis. The compound exhibited the UV (λ_{max} 252 nm, $\epsilon = 8050$) and IR (ν_{C-C} 3030, 1680 and 1620 cm^{-1}) absorption band attributable to an α,β-unsaturated ketone group, and also the ^1H NMR spectrum showed the presence of the following functional groups: three tertiary Me's (δ 0.91, 0.94 and 0.96, each 3H, s), an isolated methine (δ 2.06, 1H, sharp s), a pair of mutually coupled methines (δ 2.46 and 2.63, each 1H, dd, J = 6.5 and 1.5 Hz) and a β-methyl-α,β-unsaturated ketone group (δ 1.98, 3H, d, J = 1.5 Hz and δ 5.61, 1H, sext, J = 1.5 Hz). The above spectral data suggested that it contains a part structure of verbenone (10) or a closely related system as well as mustakone.[16] The partial structure of vulgarone B was obtained by comparison of the ^1H NMR spectra and the aromatic solvent effects with those of verbenone (10)[17] as shown in Table 4: signals of a pair of double doublets (H-1 and H-5), and a Me (H-8) and a proton (H-3) on a double bond showed a good correspondence mutually in the magnitude of the induced shifts. Besides, irradiation of the olefinic Me at δ 1.98 reformed the sextet of the olefinic proton at δ 5.61 into a triplet (J = 1.5 Hz). Reversely, irradiation of the olefinic proton at δ 5.61 changed the doublet of the olefinic Me (1.98) into a singlet and simultaneously a pair of double doublets due to the two methines (2.46 and 2.63) into a pair of doublets with a large 4-bond mutual coupling (J = 6.5 Hz) between H-1 and H-5, while a sharp singlet at δ 2.06, which showed no change on the irradiation, was

Table 5. ^1H NMR spectra (δ in ppm) of the alcohol (8) and *cis*-verbenol (13)

	$CDCl_3$		C_5D_5N	
	$(8)^a$	$(13)^b$	(8)	(13)
H-1	2.04 (dd)	1.96 (ddd)	2.07	1.91
H-3	5.33 (m)	5.36 (m)	5.60	5.59
H-4	4.38 (m)	4.44 (m)	4.72	4.73
H-5	2.37 (ddd)	2.28 (ddd)	2.53	2.41
H-7		α 1.30 (d)		α 1.33
		β 2.44 (ddd)		β 2.41
H-8	1.73 (t)	1.72	1.74	1.70
H-9	1.06 (s)	1.08	1.33	1.32
H-10		1.35 (s)		1.34
H-14	0.83 (s)	-	0.81	-
H-15	0.89 (s)	-	0.89	-

[a] All the couplings were confirmed by decoupling experiments: $J_{1,5}=6.0$; $J_{1,3}=J_{3,8}=J_{4,8}=1.5$; $J_{3,4}=J_{4,5}=3.0$ Hz.

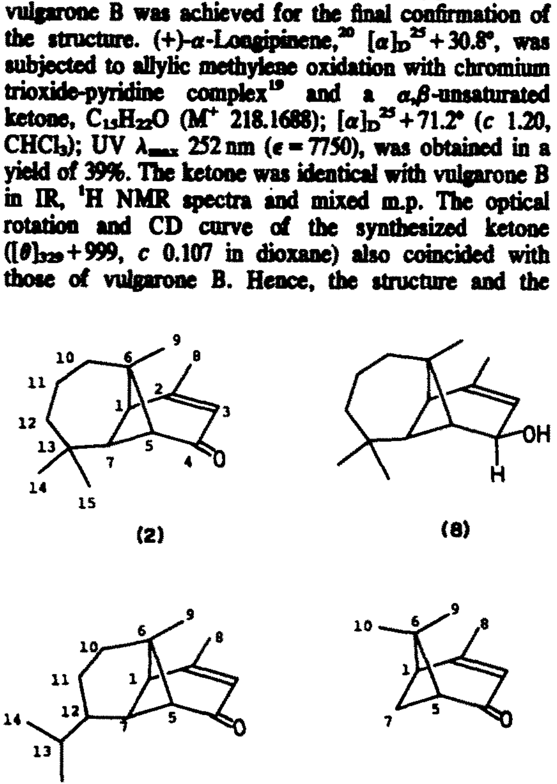
[b] The couplings are almost the same as those in ref. 13.

assigned to H-7 proton since only the α-configuration made a dihedral angle of ca. 90° with both H-1 and H-5 as well as the carbinyl proton of *cis*-chrysanthenol (7). These results support the assumption that vulgarone B contains the framework of verbenone as a partial structure, the existence of which was further confirmed by the following comparison of an alcohol (8) with *cis*-verbenol.[17]

Vulgarone B was reduced with LAH to give only a secondary alcohol (8), $C_{15}H_{24}O$, m.p. 48.5–50.0° (3,5-dinitrobenzoate, m.p. 205.0–206.0°), which had a close resemblance to *cis*-verbenol[17] in most of the peaks of the ^1H NMR spectra, especially, the one taken in C_5D_5N as shown in Table 5. The newly formed carbinyl proton at δ 4.38 (1H, m) in $CDCl_3$, on irradiation of the olefinic Me at δ 1.73; changed into a triplet (J = 3.0 Hz) as in that of *cis*-verbenol. In order to clarify the remaining portion of the structure of vulgarone B, 4-oxo-α-ylangene (9), a diastereoisomer of mustakone,[16] was synthesized by oxidation of α-ylangene[18] with chromium trioxide-pyridine complex[19] and the ^{13}C NMR spectrum was determined.

When the ^{13}C NMR spectrum of vulgarone B was compared with that of 4-oxo-α-ylangene (9) and that of verbenone (10), good correspondence was recognized as seen in Table 1, except that the two methines (C-7 and C-10) of vulgarone B were respectively replaced by a methylene and a tertiary Me in verbenone and the methylene (C-12) and quartanary carbon (C-13) by two methines in 4-oxo-α-ylangene (9). Based on this evidence, vulgarone B was considered to be a tricyclic structure (2), with an additional isoprene unit between C-7 and C-10 of the framework of verbenone (10), that is, the structure is 4-oxo-α-longipinene.

Thus, the direct conversion of α-longipinene into vulgarone B was achieved for the final confirmation of the structure. (+)-α-Longipinene,[20] $[\alpha]_D^{25}+30.8°$, was subjected to allylic methylene oxidation with chromium trioxide-pyridine complex[19] and a α,β-unsaturated ketone, $C_{15}H_{22}O$ (M^+ 218.1688); $[\alpha]_D^{25}+71.2°$ (c 1.20, $CHCl_3$); UV λ_{max} 252 nm ($\epsilon = 7750$), was obtained in a yield of 39%. The ketone was identical with vulgarone B in IR, ^1H NMR spectra and mixed m.p. The optical rotation and CD curve of the synthesized ketone ($[\theta]_{329}+999$, c 0.107 in dioxane) also coincided with those of vulgarone B. Hence, the structure and the absolute configuration of vulgarone B are as shown in formula 2.



(2) (8)

(9) (10)

Fig. 2.

Transformation of vulgarone B to vulgarone A. It has been reported that verbenone (10) was transformed into chrysanthenone (5) via 1,3-sigmatropic shift of an alkyl bonding in photochemical reaction.[21] Since vulgarone B (2) and A (1) were respectively characterized to be analogous to verbenone (10) and chrysanthenone (5) as mentioned above, it was decided to convert vulgarone B into vulgarone A. Vulgarone B(2) was irradiated in isooctane with a mercury arc lamp for 1.5 hr to give a β,γ-unsaturated cyclobutanone derivative, $C_{15}H_{22}O$ ($\nu_{C=O}$ 1780 cm^{-1}); $[\alpha]_D^{25}+132.0°$ (c 2.70, $CHCl_3$); UV λ_{max} 292 nm ($\epsilon = 101$), in a good yield, whose identity with vulgarone A was confirmed by IR, ^1H NMR, MS and ORD spectra. The structure of vulgarone A was also established as the novel skeletal tricyclic sesquiterpene ketone (1).

Vulgarone A (1) and B (2), which are higher analogs of chrysanthenone (5) and verbenone (10) by one isoprene unit, may be biogenetically synthesized using α-longipinene as a possible precursor in the plant.

EXPERIMENTAL

M.ps and b.ps are uncorrected. UV spectra were recorded in EtOH on a Hitachi 124 spectrometer and IR spectra in CCl_4 on a Hitachi EPI-G3 spectrometer. ^1H NMR spectra were recorded on a Hitachi R-22 (90 MHz) spectrometer using TMS as an internal standard, unless otherwise mentioned, in CCl_4 and ^{13}C NMR spectra on a JEOL-FX-60 spectrometer operating at 15.10 MHz in $CDCl_3$. Conventional mass spectra were obtained on a Hitachi RMS-4 spectrometer and exact mass measurements on a Hitachi RMU-7L spectrometer. CD and ORD curves were measured on a JASCO ORD/UV-5 spectrometer, equipped with the CD attachment. Analytical TLC was performed on silica gel G (E. Merck, No. 7731) and preparative TLC on silica gel PF_{254} (E. Merck, No. 7747) by using two kinds of thickness, 0.25 and 0.50 mm, respectively. Column chromatography depended on silica gel 60 (E. Merck, No. 7734) or alumina (E. Merck, No. 1097, activity II–III). GLC was carried out with a separation column (3 mm × 2 m) packed with 3% PEG-20 M or SE-30 on Chromosorb AW (60–80 mesh).

Collection of the essential oil. Chrysanthemum vulgare for the present investigation has been transplaned from the Marburg botanical garden of West Germany to the experimental garden of Hiroshima University in 1955. The aerial part of the plant was collected in July 1975 prior to the efflorescence. After being dried in the shade for one day, the material (20.0 kg) was steam distilled to obtain the essential oil (17.9 g) together with ether extract from the distilled aqueous layer in a yield of 0.089%. $[\alpha]_D^{25}-1.035°$, n_D^{25} 1.4619, d_4^{25} 0.9370.

Isolation of vulgarone A (1), *vulgarone B* (2) *and chrysanthenone* (5). The essential oil (10.0 g) was fractionated through a small size spinning band distillation column (6 × 50 cm) under reduced pressure until low-boiling fraction (b.p. 40–70°/2 Torr, 5.5 g) was distilled out.

The low-boiling fraction was chromatographed over a silica gel column using n-hexane–AcOEt (v/v, 5:1) to afford a large amount of chrysanthenone as a colorless oil. $C_{10}H_{14}O$ (M^+ 150), $[\alpha]_D^{25}-55.2°$ (c 1.50, $CHCl_3$). The IR and ^1H NMR spectra were superimposable on the authentic spectra.[15]

The remaining high-boiling fraction (4.0 g), which contained new ketones, was eluted over a silica gel column using petroleum ether–ether (v/v, 3:1). The quickly eluted portion, which showed one major spot on tlc, was further purified by chromatography over silica gel using n-hexane–$CHCl_3$ (v/v, 1:1) and vulgarone A was obtained as a colorless oil in a homogeneous state for glc. IR ν 3040, 1780, 1650, 1390, 1385, 1370 and 830 cm^{-1}; ^1H NMR see Table 2; MS *m/e* 218.1653 (M^+, 15%, $C_{15}H_{22}O$ requires: 218.1669), 203 (2), 190 (20), 175 (13), 161 (5), 148 (7), 147 (15), 135 (6), 134 (7), 133 (12), 121 (25), 120 (39), 119 (100), 108 (25), 107 (32), 106 (50) and 105 (48).

The slowly eluted portion, which showed one major spot on tlc, was purified by preparative tlc on silica gel using *n*-hexane–$CHCl_3$ (v/v, 1:3) and vulgarone B was separated as colorless needles. IR ν 3045, 1680, 1620, 1395, 1375, 1365 and 840 cm^{-1}; CD (*c* 0.107, dioxane) $[\theta]_{370}$ 0, $[\theta]_{360}+386$, $[\theta]_{355}+399$, $[\theta]_{342}+853$, $[\theta]_{336}+786$, $[\theta]_{329}+906$, $[\theta]_{328}+692$, $[\theta]_{318}+694$, $[\theta]_{304}+413$, $[\theta]_{275}$ 0; MS *m/e* 218.1684 (M^+, 59%, $C_{15}H_{22}O$ requires: 218.1669), 203 (30), 190 (6), 185 (6), 175 (33), 162 (26), 161 (42), 149 (36), 148 (100), 147 (78), 136 (26), 135 (56), 133 (33), 123 (21), 122 (31), 121 (47), 119 (33), 110 (30), 109 (41), 108 (38), 107 (33) and 105 (46). (Found: C, 82.22; H, 10.20. $C_{15}H_{22}O$ requires: C, 82.51; H, 10.16%). Semicarbazone (Found: C, 69.48; H, 9.16; N, 15.26. $C_{16}H_{25}N_3O$ requires: C, 69.78; H, 9.15; N, 15.26%).

Epoxidation of vulgarone A. To a soln of the ketone (45 mg) in CH_2Cl_2 (10 ml) anhyd Na_2CO_3 in suspension (40 mg), a soln of *m*-chloroperbenzoic acid (100 mg) in CH_2Cl_2 (5 ml) was added drop by drop at 0° during 20 min. The mixture, after being diluted with $CHCl_3$ (20 ml), was washed with 5% NaOH and water, dried over Na_2SO_4 and concentrated *in vacuo* to afford a crystalline substance, which was purified by a short column of neutral alumina using $CHCl_3$ to yield vulgarone A epoxide (3) as colorless needles (42 mg), m.p. 105.5–106.5°, $[\alpha]_D^{25}-94.2°$ (c, 0.52, $CHCl_3$): IR ν 3000, 1795, 1390, 1380, 1370, 1140 and 850 cm^{-1}; ^1H NMR δ 0.99, 1.11 and 1.18 (each 3H, s, three tertiary Me's), 1.44 (3H, s, epoxide Me), 1.50–2.00 (6H, m, three methylenes), 2.08 (1H, br.s, Wh/2, 4.0 Hz, H-4), 2.52 (1H, ddd, $J_{1,5}=6.5$; $J_{4,5}=2.0$; $J_{3,5}=1.5$ Hz, H-5), 2.71 (1H, d, $J_{1,5}=6.5$ Hz, H-1), 3.01 (1H, br.s., Wh/2, 3.0 Hz, epoxide methine), decoupling experiments: δ $3.01 \rightarrow 2.52$ (dd, J = 6.5 and 2.5 Hz) and 2.08 (d, J = 2.0 Hz), $2.52 \rightarrow 3.01$ (s) and 2.08 (s); MS *m/e* 234.1613 (M^+, 6%, $C_{15}H_{22}O_2$ requires: 234.1619), 219 (7), 206 (6), 190 (23), 175 (15), 163 (7), 151 (8), 149 (10), 147 (25), 145 (12), 137 (44), 135 (22), 133 (18), 123 (17), 121 (40), 120 (35), 119 (91), 109 (29), 108 (32), 107 (69), 106 (100) and 105 (59). (Found: C, 77.05; H, 9.49. $C_{15}H_{22}O_2$ requires: C, 76.88; H, 9.46%).

Reduction of vulgarone A. To a suspension of LAH (120 mg) in dry ether (25 ml) was added an ethereal soln of the ketone (54 mg/5 ml) under stirring, and the mixture was further stirred at room temp. for 3 hr. After the excess reagent was decomposed by adding water (2 ml) slowly, the organic layer was separated from the aqueous layer and washed successively with 2% H_2SO_4, a sat $NaHCO_3$aq and water. The soln was dried over Na_2SO_4 and concentrated *in vacuo* to yield a crystalline compound, which was purified by a short column of silica gel using $CHCl_3$–2% MeOH to afford an alcohol (4) as colorless crystals (47 mg), m.p. 50.5–52.0°, $[\alpha]_D^{25}+45.9°$ (*c* 1.80, $CHCl_3$): IR ν 3520, 3350, 3030, 1645, 1390, 1375 and 1040 cm^{-1}; ^1H NMR see Table 3; MS *m/e* 220.1819 (M^+, 4%, $C_{15}H_{24}O$ requires: 220.1825), 205 (4), 203 (3), 202 (3), 191 (3), 187 (4), 177 (3), 175 (3), 163 (3), 161 (5), 149 (6), 147 (6), 145 (8), 135 (15), 133 (10), 131 (11), 121 (16), 119 (20), 117 (17), 115 (16), 109 (18), 107 (41), 105 (33), 103 (11) and 41 (100). 3,5-Dinitrobenzoate (Found: C, 63.88; H, 6.30; N, 6.77. $C_{22}H_{26}N_2O_6$ requires: C, 63.75; H, 6.32; N, 6.76%).

Reduction of vulgarone B. To a suspension of LAH (125 mg) in dry ether (25 ml) was added an ethereal soln of the ketone (57 mg/5 ml) under stirring, and the mixture was further stirred at room temp. for 3 hr. The mixture was treated as described in the reduction of vulgarone A to give 8 as colorless crystals, m.p. 48.5–50.0°, $[\alpha]_D^{25}-9.5°$ (*c* 1.80, $CHCl_3$): IR ν 3510, 3350, 3025, 1650, 1395, 1380, 1365, 1050, 1035, 1019 and 1000 cm^{-1}; ^1H NMR see Table 5. MS *m/e* 220.1840 (M^+, 39%, $C_{15}H_{24}O$ requires: 220.1826), 205 (11), 203 (6), 202 (8), 191 (4), 187 (9), 177 (12), 161 (5), 159 (16), 149 (24), 145 (14), 135 (34), 133 (20), 131 (24), 123 (27), 121 (41), 119 (25), 117 (15), 109 (47), 107 (40), 105 (35) and 41 (100). 3,5-Dinitrobenzoate (Found: C, 63.94; H, 6.43; N, 6.81. $C_{22}H_{26}N_2O_6$ requires: C, 63.75; H, 6.32; N, 6.76%).

Synthesis of vulgarone B by allylic methylene oxidation of α-longipinene. To a soln of (+)-α-longipinene (120 mg; $[\alpha]_D^{25}+30.8°$ (*c* 4.30, $CHCl_3$))[20] in CH_2Cl_2 (20 ml) was added a slurry of CrO_3-(pyridine)$_2$ complex (3.0 g)[19] in CH_2Cl_2 (7 ml) under mechanical stirring, and the mixture was further stirred for 12 hr. After the CH_2Cl_2 soln was separated, the remaining tarry material was repeatedly extracted with two 20 ml of ether. The combined soln of ether, after being added to the CH_2Cl_2 soln, was diluted with additional ether (100 ml). The resulted soln was washed successively with a sat $NaHCO_3$aq (3 × 20 ml), 5% HCl (3 × 20 ml), and again 5% $NaHCO_3$aq (20 ml) and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* gave a yellow oily substance, which was chromatographed on a short column of silica gel using *n*-hexane and then $CHCl_3$ to give starting α-longipinene (45 mg) and an α,β-unsaturated ketone (50 mg) as colorless needles, m.p. 35.5°, $[\alpha]_D^{25}-71.2°$ (*c* 1.20, $CHCl_3$): CD (*c* 0.108, dioxane) $[\theta]_{378}$ 0, $[\theta]_{360}+416$, $[\theta]_{355}+450$, $[\theta]_{342}+933$, $[\theta]_{335}+899$, $[\theta]_{328}+799$, $[\theta]_{318}+806$, $[\theta]_{304}+450$, $[\theta]_{275}$ 0; MS *m/e* 218.1695 (M^+, 39%, $C_{15}H_{22}O$ requires: 218.1669), 203 (24), 190 (5), 185 (6), 175 (29), 162 (21), 161 (36), 149 (27), 148 (81), 147 (70), 135 (47), 133 (36), 123 (15), 122 (33), 121 (46), 119 (40), 109 (40), 108 (37), 107 (35), 105 (52) and 41 (100). The IR and ^1H NMR spectra of this ketone coincided with those of naturally occurring vulgarone B.

Transformation of vulgarone B to vulgarone A. A soln of vulgarone B (74 mg) in isooctane (50 ml), which was flushed with N_2 for 1 hr before irradiation, was irradiated with a high pressure mercury arc lamp (Riko–Kagaku 100 W) in a quartz tube for 1.5 hr without sensitizer, until the characteristic UV absorption of vulgarone B disappeared from the mixture. After a small amount of polymeric substances was filtered off, the filtrate was concentrated *in vacuo* to give a yellow oil, which was chromatographed on a short column of neutral alumina using petroleum ether–ether (v/v, 5:1) to afford an β,γ-unsaturated ketone (59 mg) as an oily substance in a homogeneous state for glc. ORD (*c* 0.20, isooctane) $[\phi]_{307}$ 8720, $[\phi]_{291}$ 0, $[\phi]_{273}+4700$, a = 134.2; MS *m/e* 218.1688 (M^+, 17%, $C_{15}H_{22}O$ requires: 218.1669), 203 (3), 190 (18), 175 (8), 161 (3), 148 (6), 147 (12), 135 (7), 133 (8), 121 (24), 120 (30), 119 (100), 108 (28), 107 (21), 106 (30) and 105 (35). The IR and ^1H NMR spectra coincided with those of naturally occurring vulgarone A.

Preparation of chrysanthenone epoxide and cis-*chrysanthenol.* Both compounds were prepared from the co-occurring (−)-chrysanthenone by treating respectively with *m*-chloroperbenzoic acid and LAH.

Chrysanthenone epoxide (6), $[\alpha]_D^{25}-93.7°$ (*c* 2.40, $CHCl_3$): IR ν 1790, 1385, 1375, 1180 and 850 cm^{-1}; ^1H NMR δ 1.13 and 1.30 (each 3H, s, gem-dimethyls), 1.38 (3H, s, epoxide Me), 2.20–2.40 (3H, m, α proton to CO and methylene), 2.69 (1H, ddd, J = 7.0, 2.5 and 2.5 Hz, α proton to CO, H-5), 3.06 (1H, br.s, epoxide methine); MS *m/e* 166.0991 (M^+, 12%, $C_{10}H_{14}O_2$ requires: 166.0992), 151 (3), 138 (3), 123 (7), 122 (21), 108 (12), 107 (100) and 105 (14).

cis-*Chrysanthenol* (7), $[\alpha]_D^{25}+40.8°$ (*c* 2.60, $CHCl_3$): IR (neat) ν 3300, 3020, 1650, 1385, 1365, 1175, 1070, 1030 and 785 cm^{-1}; ^1H NMR see Table 3; MS *m/e* 152.1211 (M^+, 35%, $C_{10}H_{16}O$ requires: 152.1220), 137 (23), 135 (11), 123 (21), 121 (50), 120 (12), 119 (29), 109 (72), 108 (16), 107 (58), 105 (23) and 81 (100).

Oxidation of α-ylangene to 4-oxo-α-ylangene. (+)-α-Ylangene (250 mg; $[\alpha]_D^{25}+56.0°$ (*c* 1.88, $CHCl_3$))[18] was oxidized with CrO_3-(pyridine)$_2$ complex as in the case of α-longipinene to give (+)-oxo-α-ylangene (9) as an oily substance (110 mg), $[\alpha]_D^{25}+90.6°$ (*c* 1.17, $CHCl_3$): IR ν 3045, 1680, 1630, 1390, 1380 and 845 cm^{-1}; ^1H NMR δ 0.89 (6H, d, J = 6.0 Hz, isopropyl Me's), 0.93 (3H, s, bridgehead Me), 1.40–1.90 (6H, m, three methylenes), 1.98 (3H, d, J = 1.5 Hz, olefinic Me), 2.12 (1H, dd, J = 7.0 and 1.5 Hz, H-1), 2.40 (1H, dd, J = 7.0 and 1.5 Hz, H-5), 2.53 (1H, s, H-7), 5.64 (1H, sext, J = 1.5 Hz, olefinic proton); MS *m/e* 218.1690 (M^+, 56%, $C_{15}H_{22}O$ requires: 218.1669), 203 (32), 190 (7), 189 (12), 185 (5), 175 (71), 161 (41), 159 (16), 157 (25), 149 (25), 148 (75), 147 (100), 145 (20), 135 (43), 134 (24), 133 (72), 131 (21), 123 (24), 122 (74), 121 (41), 120 (21), 119 (53), 117 (26), 115 (27), 110 (36), 109 (35), 108 (32), 107 (36), 106 (25) and 105 (85).

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[17] Verbenone: $[\alpha]_D^{25}+91.8°$ (c 4.20, $CHCl_3$); UV λ_{max} 252 nm ($\epsilon = 8850$, EtOH). *cis*-Verbenol: m.p. 67.0–68.0°; $[\alpha]_D^{25}+7.5°$ (c 1.73, $CHCl_3$). These two compounds were prepared from (+)-α-pinene ($[\alpha]_D^{25}+23.4°$) by CrO_3 oxidation reported in Ref. 19 and successive LAH reduction.

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