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VULGARONE B, A NOVEL SESQUITERPENE KETONE FROM *CHRYSANTHEMUM BULGARE* AND ITS PHOTOCHEMICAL TRANSFORMATION TO VULGARONE A

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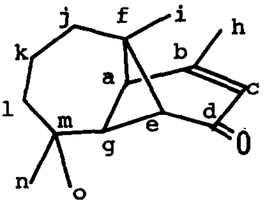
In our course of investigation on the essential oil of *Chrysanthemum vulgare* (L.) Bernh., a medicinal plant, we now isolated a novel sesquiterpene ketone, which was named vulgarone B, and whose structure was elucidated to be 2,6,6,11-tetramethyltricyclo[5.4.0.$0^{2,8}$]undec-10-en-9-one (1). In the photochemical examination, furthermore, this ketone was converted to vulgarone A (2)[1] in a good yield accompanied by some minor products.

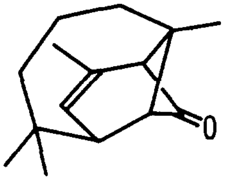
Vulgarone B, mp 35.5-36.0°; $[\alpha]_D$ +63.4° (c 1.10, $CHCl_3$); CD(Dioxane) $[\theta]_{329}$ +906, isolated from the steam-volatile oil, was determined to have a molecular formula of $C_{15}H_{22}O$ (M^+ 218.1684, calc. 218.1670) and it was characterized as an α,β-unsaturated ketone based on the UV (λ_{max}^{EtOH} 252 nm, ε=8050) and IR ($\nu_{max}^{CCl_4}$ 3030, 1680, 1620 cm^{-1}) absorption bands. The ^{13}C-NMR($CDCl_3$) and ^{1}H-NMR(CCl_4) spectra revealed the presence of the following functional groups: a trisubstituted double bond which contained a methyl group (δC 172.4, s, δC 122.5, d; δH 5.61, 1H, sext, J=1.5 Hz. δC 22.9, q; δH 1.98, 3H, d, J=1.5 Hz) and was conjugated with the ketone group (δC 204.7, s), an isolated methine (δC 58.0, d; δH 2.06, 1H, s), two methines (δC 50.0, d, δC 66.8, d; δH 2.46, 1H, d.d, J=6.5, 1.5 Hz, δH 2.63, 1H, d.d, J=6.5, 1.5 Hz) showing similar couplings to the two methine protons of verbenone (4),[2] a gem-dimethyl (δC 33.8, s, δC 27.3, q, δC 27.8, q; δH 0.91, 3H, s, δH 0.94, 3H, s) and a tertiary methyl (δC 55.1, s, δC 23.6, q; δH 0.96, 3H, s). Irradiation of the olefinic methyl at δ 1.98 reformed the sixtet of the olefinic proton at δ 5.61 into a triplet (J=1.5 Hz).

Reversely, irradiation of the olefinic proton (δ 5.61) reformed the doublet of the olefinic methyl (δ 1.98) into a singlet and further two double doublets of both methines (δ 2.46 and δ 2.63) into two doublets (J=6.5 Hz). The above spectral properties of vulgarone B closely resembled those of verbenone (4)[2] and mustakone.[3]

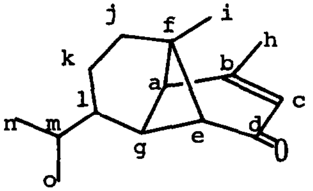
In the reduction with LAH in abs. Et_2O, vulgarone B afforded an allylic secondary alcohol (δ 4.38, 1H, m, -C$\underline{H}$(OH), δ 1.91, s, -OH), $C_{15}H_{24}O$ (M^+ 220.1840, calc. 220.1826); mp 48.5-50.0°; $[\alpha]_D$ -9.5° (c 1.80, $CHCl_3$); 3,5-DNB, mp 205.0-206.0°, which held a trisubstituted double bond containing a methyl group (δ 1.73, 3H, t, J=1.5 Hz, δ 5.33, 1H, m), two methines (δ 2.04, 1H, d.d, J=6.0, 1.5 Hz, δ 2.37, 1H, d.d.d, J=6.0, 3.0, 1.5 Hz) which coupled with an olefinic proton (J=1.5 Hz) or a carbinol proton (J=3.0 Hz) and the olefinic proton (J=1.5 Hz)



(1)



(2)



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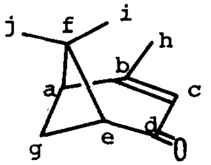

(4)

Table. Comparison of the ^{13}C-NMR*1

assignment	vulgarone B(1)	α-ylangene ketone(3)	verbenone(4)*2
a	50.0(d)	46.6(d)	49.6(d)
b	172.4(s)	169.2(s)	169.8(s)
c	122.5(d)	122.1(d)	121.0(d)
d	204.7(s)	202.7(s)	203.2(s)
e	66.8(d)	64.1(d)	57.5(d)
f	55.1(s)	56.6(s)	53.7(s)
g	58.0(d)	56.2(d)	40.6(t)
h	22.9(q)	20.3(q)	21.9(q)
i	24.7(q)	23.8(q)	23.4(q)
j	38.6(t)	36.6(t)	26.5(q)
k	21.4(t)	22.1(t)	
l	41.6(t)	44.9(d)	
m	33.8(s)	31.9(d)	
n	27.3(q)	19.4(q)	
o	27.8(q)	19.6(q)	

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*1 The spectra were taken in $CDCl_3$ on JEOL-FX60 spectrometer; Chemical shift(δC) are given in ppm relative to TMS.

*2 The assignment : L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley Interscience, New York, N. Y., 1972, spectrum no. 387.

together with the mutual coupling, and each of tertiary methyl (δ 1.06, 3H, s) and gem-dimethyl (δ 0.83 and δ 0.89, each 3H, s). Irradiation of the olefinic methyl at δ 1.73 of the alcohol caused the multiplet of the carbinol proton (δ 4.38) to change into a triplet (J=3.0 Hz).

When the ^{13}C-NMR and ^{1}H-NMR spectra of vulgarone B (1) and the above alcohol were respectively compared with those of α-ylangene ketone (3),[4] verbenone (4) and *cis*-verbenol which have a common partial structure of bicyclo[3.1.1]heptane nucleus, a good correspondence was recognized as shown in Table which listed ^{13}C-NMR spectra of these ketones merely. On the basis of the above results, vulgarone B was assigned to the tricyclic structure (1) holding an additional isopentane unit between C-g and C-j in the molecule of verbenone (4).

The final confirmation of this structure was given by successful preparation of vulgarone B in the oxidation of (+)-α-longipinene,[5] $[\alpha]_D$ + 30.8° (c 4.30, $CHCl_3$) with CrO_3-(pyridine)$_2$ complex[6] in CH_2Cl_2. An α,β-unsaturated ketone, $C_{15}H_{22}O$ (M^+ 218.1695, calc. 218.1670); mp 35.5-36.0°; $[\alpha]_D$ +71.2° (c 1.20, $CHCl_3$) ; λ_{max}^{EtOH} 252 nm, ε=7750; CD(Dioxane) $[\theta]_{329}$ +999, thus obtained in 39% yield, showed no depression in mixed melting point determination with natural vulgarone B (1) and a good agreement in IR, ^{1}H-NMR and optical rotation. Accordingly, the structure and the absolute configuration of vulgarone B should be represented by formula (1).

In addition, the photochemical transformation of vulgarone B was examined by irradiation with 100W mercury arc lamp in isooctane. After 1.5 hr, vulgarone B was converted to a β,γ-unsaturated cyclobutanone, $C_{15}H_{22}O$ (M^+ 218); $[\alpha]_D$ +132.0° (c 2.70, $CHCl_3$); λ_{max}^{EtOH} 292 nm, ε=101; ORD $[\phi]_{307}$ +8720, $[\phi]_{290}$ 0, $[\phi]_{273}$ -4700, a=134 (isooctane), in 80% yield, which was identical with natural vulgarone A (2) in IR, ^{1}H-NMR and ORD. This transformation of vulgarone B to A is one example for the [1,3]-sigmatropic shift of an alkyl bonding in photorearrangement of the α,β-unsaturated ketone.[7]

Co-occurrence of vulgarone A and B, which are higher analogs by one isoprene unit to chrysanthenone and verbenone, and which are connected through the photochemical transformation, is of interest in the biogenesis of these compounds.

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References and Notes

(1) Y. Uchio, A. Matsuo, M. Nakayama and S. Hayashi, Tetrahedron Lett., 1976, 2963; vulgarone in the previous communication was renamed vulgarone A because of being correlated to vulgarone B in this communication.

(2) M. A. Cooper, J. R. Salmon, D. Whittaker and U. Scheidegger, J. Chem. Soc. (B), 1967, 1259.

(3) V. H. Kapadia, B. A. Nagasampagi, V. G. Naik and Sukh Dev, Tetrahedron Lett., 1963, 1933.

(4) According to a method reported by W. Dauben (ref. 6), the (+)-α-ylangene ketone was prepared from (+)-α-ylangene. The (+)-α-ylangene was kindly provided by Drs. Y. Ohta and K. Morikawa, The Institute of Food Chemistry, Mishima, Osaka, Japan.

(5) H. Erdman and L. Westfelt, Acta. Chem. Scand., 17, 2351 (1963); (+)-α-longipinene was isolated from Chinese terpentine oil. We are indebted to Yasuhara Perfumery Co. Ltd., for gift of the oil and Prof. A. Yoshikoshi and Dr. M. Miyashita, Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, for supplying the IR and ^{1}H-NMR spectra of α-longipinene.

(6) W. Dauben, M. Lorber and D. S. Fulierton, J. Org. Chem., 34, 3587 (1969).

(7) D. I. Schuster and D. Widman, Tetrahedron Lett., 1971, 3571 and refs. cited therein.