BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1565 (1973)

The Isolation of *trans*-Chrysanthenyl Acetate and Chrysanthenone from the Essential Oil of *Chrysanthemum shiwogiku*

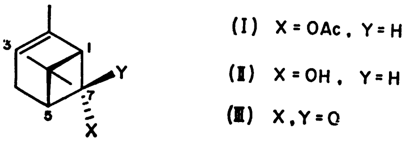
Akihiko Matsuo, Yasuto Uchio, Mitsuru Nakayama, and Shûichi Hayashi
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda, Hiroshima 730

(Received September 12, 1972)

In the course of our chemosystematic investigation of *Crysanthemum* species native in Japan, the essential oil of *Chrysanthemum shiwogiku* Kitam. (Japanese name, Shiogiku; chromosomes, 2n=72) was examined, (+)-*trans*-chrysanthenyl acetate being isolated as the major component (23.2%). Furthermore, seven monoterpenoids containing (+)-chrysanthenone (2.1%) were isolated, and the occurrence of a trace of *trans*-chrysanthenol was confirmed gas chromatographically. Although (+)-chrysanthenone[1] and (−)-*cis*-chrysanthenyl acetate[2] have been previously isolated from other plants of the same *Chrysanthemum*, and (−)-*trans*-chrysanthenol has been synthesized from (−)-α-pinene by Joulain and Rouessac[3] immediately after the present investigation was carried out, (+)-*trans*-chrysanthenyl acetate has not yet been synthesized, nor has it been isolated in nature.

Experimental

The essential oil ($[\alpha]_D$ −11.7°, n_D 1.4830, d_4 0.9395) was obtained by the steam-distillation of stalks and leaves of the plants collected beside the sea at Maruyama in Muroto City in a 0.06% yield of the fresh plants. It was subjected to fractional distillation at reduced pressure and then to silica gel elution chromatography with a mixed solvent of hexane and ethyl acetate (4 : 1) in order to isolate each component.



Chart

Results and Discussion

*(+)-*trans*-Chrysanthenyl Acetate (I).* The main component ($[\alpha]_D$ +32.0°, 1.75% in $CHCl_3$; n_D 1.4666) has $C_{12}H_{18}O_2$ (M^+ 194). The IR and NMR spectra exhibited a geminal dimethyl (ν_{max}^{liq} 1375 and 1360 cm^{-1}; $\delta_{ppm}^{CCl_4}$ 0.88 and 1.25, each 3H, s), a trisubstituted double bond containing a methyl group (ν 795 cm^{-1}; δ 1.57, 3H, q, J=2.0 Hz and 5.30, 1H, m), and a methine proton (δ 4.87, 1H, t, J=6.0 Hz) bearing an acetoxy residue (ν 1740, 1248, and 1035 cm^{-1}; δ 1.88, 3H, s). Since the NMR spectrum closely resembled that of α-pinene[4] except for the singlet at δ 1.88 and the triplet at δ 4.87, the compound could be characterized as the acetate of a hydroxyl derivative of α-pinene. When this acetate was treated with lithium aluminium hydride in dry ether, it underwent reduction and was converted into a secondary alcohol (II) ($C_{10}H_{16}O$; $[\alpha]_D$ −55.0°, 1.04% in $CHCl_3$; 3.5-DNB, mp 112—113°C; ν_{max}^{liq} 3450, 1085 and 795 cm^{-1}), whose NMR spectrum ($\delta_{ppm}^{CCl_4}$ 0.87 and 1.22, each 3H, s; 1.68, 3H, q, J=2.0 Hz; 4.20, 1H, t, J=6.0 Hz; 5.51, 1H, m) was in a good agreement with that of the (−)-*trans*-chrysanthenol (II) synthesized lately from (−)-α-pinene.[3] Especially, the coupling constant (t, J=6.0 Hz) of the C_7-methine proton signal showed the alcohol to be of the *trans*-form. The secondary alcohol (II) was further oxidized with a Conforth reagent in pyridine to give a unique four-membered ring ketone (III), ($[\alpha]_D$ +63.8°, 0.26% in $CHCl_3$; ν_{max}^{liq} 1780, 1380, 1370, 790, and 740 cm^{-1}; $\delta_{ppm}^{CCl_4}$ 1.20 and 1.23, each 3H, s; 1.73, 3H, q, J=2.0 Hz; 5.31, 1H, m), whose IR and NMR spectra coincided with those of (+)-chrysanthenone.[5] Therefore, it was concluded that the original compound was the (+)-*trans*-chrysanthenyl acetate.

(+)-Chrysanthenone (III) and trans-*Chrysanthenol (II).* A ketone ($[\alpha]_D$ +30.0°, 0.30% in isooctane) was isolated through silica gel elution chromatography: its IR and NMR spectra coincided with those of the chrysanthenone obtained from the chrysanthenyl acetate as described above. In the gas chromatography of the essential oil, a small peak corresponding to *trans*-chrysanthenol was detected by the use of SE-30 and PEG-6000 columns, but further identification was not attempted.

Other Constituents. From the essential oil, α-pinene (0.8%), camphene (2.3%), sabinene (1.0%), *p*-cymene (12.7%), camphor (10.9%), borneol (5.5%), bornyl acetate (2.8%), α-copaene (0.3%), β-elemene (1.4%), β-caryophyllene (2.9%), ε-cadinene (5.7%), and caryophyllene oxide (1.3%), in addition to the above α-pinene derivatives, (+)-*trans*-chrysanthenyl acetate (23.3%), *trans*-chrysanthenol (trace) and (+)-chrysanthenone (2.1%), were isolated and identified by IR, NMR, and mass spectrometries.

The authors are indebted to Professor Ryûso Tanaka, Department of Botany, Hiroshima University, for collecting and identifying the plant material.

---

1) A. R. Penfold, E. R. Ramage and J. L. Simonsen, *J. Chem. Soc.*, **1939**, 1496; E. P. Blanchard, *Chem. Ind.*, **1958**, 293; M. Kotake and H. Nonaka, *Ann. Chem.*, **607**, 153 (1957).

2) J. T. Pinhey and I. A. Southwell, *Aust. J. Chem.*, **34**, 1311 (1971).

3) D. Joulain and F. Rouessac, *Chem. Commun.*, **1972**, 314.

4) Varian Associates, "Nuclear Magnetic Resonance Spectra Catalog," Vol. 1, Varian Associates, Palo Alto, Cal., (1962). p. 272.

5) The IR and NMR spectra were kindly supplied by Dr. H. Chikamatsu, Osaka University and Dr. J. T. Pinhey, Sydney University.