

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

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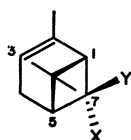
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In the course of our chemosystematic investigation of *Chrysanthemum* species native in Japan, the essential oil of *Chrysanthemum shiwogiku* Kitam. (Japanese name, Shiogiku; chromosomes, $2n=72$) was examined, (+)-*trans*-chrysanthenyl acetate being 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 (+)-chrysanthenone¹⁾ and (–)-*cis*-chrysanthenyl acetate²⁾ have been previously isolated from other plants of the same *Chrysanthemum*, and (–)-*trans*-chrysanthenol has been synthesized from (–)- α -pinene by Joulain and Rouessac³⁾ 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 ($[\alpha]_D -11.7^\circ$, $n_D 1.4830$, $d_4 0.9395$) 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.



(I) X = OAc, Y = H

(II) X = OH, Y = H

(III) X, Y = O

Chart

Results and Discussion

(+)-*trans*-Chrysanthenyl Acetate (I). The main component ($[\alpha]_D +32.0^\circ$, 1.75% in CHCl_3 ; $n_D 1.4666$) has $\text{C}_{12}\text{H}_{18}\text{O}_2$ ($M^+ 194$). The IR and NMR spectra exhibited a geminal dimethyl ($\nu_{\text{max}}^{\text{liq}}$ 1375 and 1360 cm^{-1} ; $\delta_{\text{ppm}}^{\text{CCl}_4}$ 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) bear-

ing an acetoxy residue (ν 1740, 1248, and 1035 cm^{-1} ; δ 1.88, 3H, s). Since the NMR spectrum closely resembled that of α -pinene⁴⁾ 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) ($\text{C}_{10}\text{H}_{16}\text{O}$; $[\alpha]_D -55.0^\circ$, 1.04% in CHCl_3 ; 3.5-DNB, mp 112–113°C; $\nu_{\text{max}}^{\text{liq}}$ 3450, 1085 and 795 cm^{-1}), whose NMR spectrum ($\delta_{\text{ppm}}^{\text{CCl}_4}$ 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 C₇-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), ($[\alpha]_D +63.8^\circ$, 0.26% in CHCl_3 ; $\nu_{\text{max}}^{\text{liq}}$ 1780, 1380, 1370, 790, and 740 cm^{-1} ; $\delta_{\text{ppm}}^{\text{CCl}_4}$ 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 ($[\alpha]_D +30.0^\circ$, 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.

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

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