Moreover, as shown in Fig. 1, **4a** in lower oral dose of 0.3 mg/kg inhibited significantly the pressor response to AI (310 ng/kg, *i. v.*) of unanesthetized rats. The inhibitory activities of **4a** *in vitro* and *in vivo* were almost same as those of **8**. These data suggest the usefulness of **4a** as a diagnostic or therapeutic agent for the renal hypertensive disease. In addition, structure activity relationship restricted to mercaptoacyl moiety of the thiazolidine derivatives was as follows: 3-mercapto-2-methylpropanoyl>2-mercaptopropanoyl>3-mercaptopropanoyl>3-mercaptobutanoyl>4-mercaptobutanoyl. In this respect, further evaluation is now in progress.

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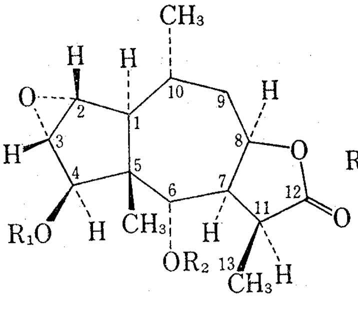
Isolation and Structure Determination of 4-*O*-Tigloyl-11,13-dihydroautumnolide, a New Sesquiterpene Lactone from North Carolina *Helenium autumnale* L.

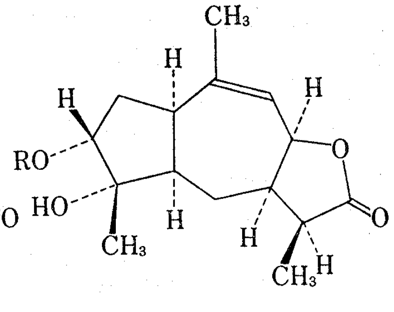
The structure and relative stereochemistry of 4-*O*-tigloyl-11,13-dihydroautumnolide (I), a new pseudoguaianolide sesquiterpene lactone from North Carolina *Helenium autumnale* L., have been determined on the basis of spectroscopic data, chemical transformation, and single-crystal X-ray analysis.

Keywords——4-*O*-tigloyl-11,13-dihydroautumnolide; sesquiterpene lactone; *Helenium autumnale* L.; X-ray analysis; structure determination

As a consequence of our continuing investigations of the terpenoid fraction of an extract from *Helenium autumnale* L. collected in North Carolina, U. S. A.,[1] we here report on the iso-



I : R_1= tiglyl, R_2=H
IV : R_1= tiglyl, R_2=$COCH_3$
V : R_1=R_2=H



II : R=H
III : R= angelyl

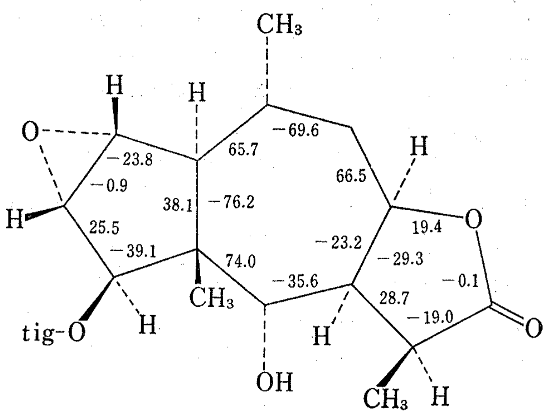


Fig. 1. Endocyclic Torsion Angles (Deg.) in (I)

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[1] A.T. McPhail, K.D. Onan, H. Furukawa, and K.H. Lee, *Tetrahedron Lett.*, **1975**, 1229; A.T. McPhail, P.A. Luhan, K.H. Lee, H. Furukawa, R. Meck, and C. Piantadosi, *Tetrahedron Lett.*, **1973**, 4087; H. Furukawa, K.H. Lee, T. Shingu, R. Meck, and C. Piantadosi, *J. Org. Chem.*, **38**, 1722 (1973).

lation and structural characterization of a new sesquiterpene lactone, 4-*O*-tigloyl-11,13-dihydroautumnolide (I).

The new lactone(I), $C_{20}H_{28}O_6$, was isolated as a minor constituent in the form of colorless needles, mp 198—199°, from the mother liquor following the removal of carolenalin(II)[1] and carolenin(III)[1] by repeated silica gel chromatography. The infrared (IR, $CHCl_3$) spectrum of I indicated the presence of a hydroxyl group (3500 cm^{-1}), a γ-lactone ring (1765 cm^{-1}), an ester function (1710 cm^{-1}), and a double bond (1645 cm^{-1}). That the ester band was due to a tiglate moiety was suggested by the mass spectral peak at (M-100) and was supported by the appearance in the ^1H nuclear magnetic resonance (NMR) spectrum ($CDCl_3$) of a broad two-methyl singlet at δ 1.84 and a one-proton multiplet at δ 6.87. The ^1H NMR spectrum also exhibited the following signals: δ 1.05 (3H, s), 1.19, 1.22 (6H, d, $J=4.0$ Hz), 3.10 (1H, d, $J=6.0$ Hz; disappeared upon addition of D_2O), 3.35 (1H, d, $J=4.0$ Hz), 3.45 (1H, d, $J=4.0$ Hz), 3.66 (1H, d, $J=6.0$ Hz; transformed into a singlet upon addition of D_2O), 4.72 (1H, br. t, $J=6.0$ Hz), 4.93(1H, br. s). In addition to containing signals for the five carbon atoms of the tiglate moiety, the ^{13}C NMR spectrum ($CDCl_3$) of I revealed the presence of three $-CH_3$, one $-CH_2-$, four >CH-, one $-\overset{|}{\underset{|}{C}}-$, five >CH-O-, and one C=O group.

Acetylation of I with acetic anhydride in pyridine at room temperature yielded a monoacetate(IV), the ^1H NMR of which showed the presence of an acetyl methyl singlet at δ 2.07, and the one-proton signal at δ 3.66 in I was shifted downfield to δ 4.90(1H, d, $J=3.0$ Hz). The ^1H NMR spectrum of crystalline(V), mp 92—93°, obtained by hydrolysis of I with 10% KOH–MeOH, indicated an upfield shift to δ 3.96 of the one-proton singlet at δ 4.93 in I; in addition, the characteristic signals associated with the tiglate ester moiety were absent. Oxidation of I with pyridinium chlorochromate gave a monoketone, the IR spectrum of which showed intense bands at 1775 and 1710 cm^{-1} and the ^1H NMR spectrum contained signals at δ 1.30 (3H, s), 1.28, 1.36 (6H, pair of doublets, $J=5.0$ Hz), 2.17 (1H, m), 2.89 (1H, quint), 3.38, 3.65 (2H, pair of doublets, $J=3.0$ Hz), 3.95 (1H, t, $J=8.0$ Hz), 4.75 (1H, sept), 4.94 (1H, br. s), and 6.88 (1H, m).

The foregoing chemical and spectral data and extensive ^1H NMR (100 MHz) decoupling experiments suggested that the structure of the new lactone was as depicted in I, *i. e.* I is the 4-*O*-tigloyl-11,13-dihydro derivative of autumnolide which was isolated by Herz *et al.*[2] from Alabama *Helenium autumnale* L. In order to establish the structure and stereochemistry unequivocally, a single-crystal X-ray analysis was undertaken. Crystals of I belong to the orthorhombic system, space group $P2_12_12_1$, with four molecules in a unit cell of dimensions $a=10.389(6)$, $b=20.341(12)$, $c=8.905(5)$ Å. The structure was solved by direct methods. Refinement of atomic positional and thermal (anisotropic C, O; isotropic H) parameters by full-matrix least-squares calculations has led to convergence at $R=0.051$ over 1750 statistically significant $[I>2.0\sigma(I)]$ reflections measured on an Enraf-Nonius CAD-3 automated diffractometer (Ni-filtered Cu-K_α radiation, $\lambda=1.5418$ Å; θ—2θ scans). Individual bond lengths and valency angles all lie in the normal ranges. Endocyclic torsion angles[3] characterizing the ring conformations are shown in the Figure. The cyclopentane and γ-lactone rings both adopt envelope conformations with C(5) and C(7) as the respective out-of-plane atoms. Analysis of derivations of the cycloheptane ring torsion angles from an ideal twist-chair form in which the C_2 axis passes through C(7) (ΔC_2-TC$=15.5°$)[4] and a chair form in which the C_s

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[2] W. Herz, P.S. Subramaniam, and N. Dennis, *J. Org. Chem.*, 34, 2915 (1969); R.B. von Dreele, G.R. Pettit, G.M. Cragg, and R.H. Ode, *J. Am. Chem. Soc.*, 97, 5256 (1975).

[3] The torsion angle A–B–C–D is defined as positive if, when viewed along the B–C bond, atom A must be rotated clockwise to eclipse atom B.

[4] $\Delta C_2-\mathrm{TC}=|\omega_{1,5}-\omega_{9,10}|+|\omega_{5,6}-\omega_{8,9}|+|\omega_{6,7}-\omega_{7,8}|$; $\Delta C_s-\mathrm{C}=|\omega_{7,8}|+|\omega_{6,7}+\omega_{8,9}|+|\omega_{5,6}+\omega_{9,10}|+|\omega_{1,5}+\omega_{1,10}|$, where the ω_{ij} are the endocyclic torsion angles about the bond between atoms i and j.

symmetry plane passes through C(1) (ΔC_s—C=69.0°) indicates that the ring conformation lies closer to the more frequently encountered, lower energy twist-chair form.[5]

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[5] A.T. McPhail and G.A. Sim, *Tetrahedron*, **29**, 1751 (1973).

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Structure of Anthriscusin, a New Phenylpropanoid Ester from the Roots of *Anthriscus sylvestris* HOFFM.

A new phenylpropanoid ester, anthriscusin was isolated from the roots of *Anthriscus sylvestris* HOFFM. (Umbelliferae), and was elucidated as O-[(*Z*)-2-angeloyloxymethyl-2-butenoyl]-3-methoxy-4,5-methylenedioxycinnamyl alcohol on the basis of the spectral data and the chemical evidence.

Keywords——anthriscusin; O-[(*Z*)-2-angeloyloxymethyl-2-butenoyl]-3-methoxy-4,5-methylenedioxycinnamyl alcohol; phenylpropanoid ester; (*Z*)-2-angeloyloxymethyl-2-butenoic acid; 3-methoxy-4,5-methylenedioxycinnamyl alcohol; crocatone; *Anthriscus sylvestris* HOFFM.

Anthriscus sylvestris HOFFM. (Umbelliferae) is a perennial herb growing in Eurasia and eastern North America. The roots of this plants had been used once as one of the chinese drug "qianhu (前胡)" and had been demonstrated to afford a lignan, anthricin(desoxypodophyllotoxin).[1] In order to examine the constituents of this plants more closely, the authors have reinvestigated this roots and have obtained a new phenylpropanoid ester(I), named anthriscusin, besides several lignans and carboxylic acid from the hexane extract. The structure of I was established as O-[(*Z*)-2-angeloyloxymethyl-2-butenoyl]-3-methoxy-4,5-methylenedioxycinnamyl alcohol on the basis of the spectral data and the chemical evidence. This paper deals with the structure elucidation of I.

I, viscous liquid, yield 0.05%, $bp_{0.25}$ 205—210°, $C_{21}H_{24}O_7$, gives a violet coloration with chromotropic acid and sulfuric acid and shows the infrared absorption bands (cm^{-1}, $CHCl_3$) at 1720, 1700 (C=O); 1643, 1625 (C=C); 1605, 1500 (aromatic ring). The proton magnetic resonance (PMR) spectrum of I exhibits the signals (δ ppm, $CDCl_3$) at 1.89 (3H, m), 1.94 (3H

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[1] T. Noguchi and M. Kawanami, *Yakugaku Zasshi*, **60**, 629 (1940).