

Table 2. Interatomic distances within the complex ion $\text{Me}(\text{CN})_6^{4-}$, Me being Fe or Mn.

Bond	d (Å), Fe	d (Å), Mn
Me—C(1)	2.04	1.93
Me—C(2)	1.90	2.00
Me—C(3)	1.98	1.89
C(1)—N(1)	1.12	1.16
C(2)—N(2)	1.21	1.13
C(3)—N(3)	1.14	1.20

shown in Fig. 1, and approximate interatomic distances within the complex ions are listed in Table 2.

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Constituents of Umbelliferous Plants

XVIII.* Terpenoids and Coumarins of the Root of *Ligusticum seguierei* Koch

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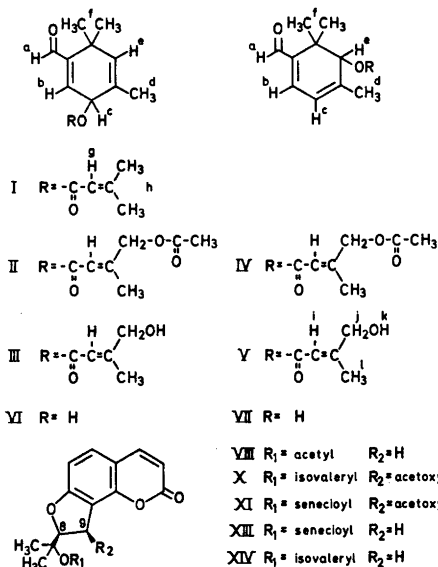
The root of *Ligusticum seguierei* Koch, in addition to several coumarins, has afforded a number of esters (I–V), derived from the terpene alcohols (VI)

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and (VII). Esters of these alcohols have recently been shown to occur in several umbellifers.^{1–3} An important feature of their chemistry is their rapid cleavage by treatment with mineral acids. In addition to the carboxylic acid liberated in this reaction, mainly 2,3,4-trimethylbenzaldehyde is formed by rearrangement of the terpenoid skeleton.

The terpene esters (II), (III), and (IV) are known from other umbelliferous plants,^{1,3} whereas (I) and (V) appeared to be new. The structures 1,1,5-trimethyl-2-formyl-4-(3-methyl-2-butenyloxy)-cyclohexadiene-(2,5) (I) and 1,1,5-trimethyl-2-formyl-6-((*E*)-3-hydroxymethyl-2-butenyloxy)-cyclohexadiene-(2,4) (V) for these compounds were deduced from the results of their acid cleavage and from comparisons of their UV-, IR-, ¹H NMR-, and mass spectra with those of their congeners.

Samples of esters of (VI) and, in particular, esters of (VII), show severe deterioration during storage. Contrary to esters of (VII), esters of (VI) show no fall in



optical activity, when regained from partly deteriorated samples by chromatography. Nevertheless compound (II), obtained from *Ligusticum seguierei*, was optically less pure than that obtained earlier from

Selinum carvifolium L.¹ Isomerization during storage of esters of (VI) into esters of (VII), or the reverse, has not been observed.

The coumarins isolated are all known. In addition to 8(*S*)-*O*-acetyl-8,9-dihydrooroseol (VIII), which to our knowledge has not previously been obtained from natural sources, umbelliprenin (spot IX, Fig. 1), 8(*S*),9(*R*)-9-acetoxy-*O*-isovaleryl-

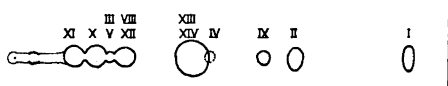


Fig. 1. Thin-layer chromatogram of the root extract. Silica gel GF₂₅₄ (Merck), petroleum ether-ether (2:1), 3-fold development. Visualization: long wave and short wave UV-light and spraying with 2,4-dinitrophenylhydrazine reagent.

8,9-dihydrooroseol (X), 8(*S*),9(*R*)-9-acetoxy-*O*-senecioid-8,9-dihydrooroseol (XI), and ostruthin (spot XII, Fig. 1) were isolated. Furthermore, a mixture of the senecioate and the isovalerate of 8(*S*)-8,9-dihydrooroseol, (XIII) and (XIV), respectively, which were virtually unseparable by chromatography, were obtained.

Experimental. Melting points, spectroscopic data, mass spectra and optical rotation values were obtained as described in previous papers (see, e.g. Ref. 1).

The plant material was grown near Copenhagen and collected in July 1967. The dried and ground roots (200 g) on extraction with ether, and subsequent evaporation of the solvent, afforded 10.3 g of extract, which was chromatographed on 230 g of silica gel.¹ The sequence of eluents was tetrachloromethane-methylene chloride (2:1), to which increasing amounts of ethyl acetate were added (1/2–25%). This fractionation divided the material into several main fractions. The aldehydes were isolated and purified by chromatography on silica gel,¹ using mainly petroleum ether, to which ether or ethyl acetate was added, as eluents. The coumarins were isolated by chromatography on silica gel,¹ using mainly the same eluents as described in a previous paper.⁴ The following compounds were obtained (described in order of elution):

a. 1,1,5-Trimethyl-2-formyl-4-(3-methyl-2-butenyloxy)-cyclohexadiene-(2,5) (I). A viscous liquid, which crystallized upon standing. White

needles, m.p. 49–51°. $[\alpha]_D^{20} +183^\circ$ (c 1.2, CCl₄). UV: λ_{max} (EtOH) 227 nm (4.42). IR: 2715, 1710 (CHO), and 1645 cm⁻¹ (C=C). ¹H NMR-data (δ -values): A singlet at 9.47 is assigned to the aldehyde proton a, a doublet at 6.50 (1H) ($J_{b,c}=4$ cps) to the proton b, a multiplet at 5.80 (1H) to the proton c, a perturbed doublet at 1.73 (3H) ($J_{c,d}=ca. 1$ cps) to the methyl protons d, a slightly broadened singlet at 5.39 (1H) to the proton e, and singlets at 1.28 and 1.22 (3H each) to the gem-dimethyl protons f. The acid moiety of (I) gives rise to a multiplet at 5.61 (1H) and two doublets at 1.94 and 2.20 (3H each) ($J_{h,g}=2$ cps), assigned to the protons g and h, respectively. Mass spectrum (sample temp. 24°): 248 (M⁺, 2½), 233 (4), 166 (20), 151 (3), 121 (9), 105 (8), 84 (6), 83 (100), 77 (5), 55 (9), 39 (6).

b. Umbelliprenin (IX), m.p. 59.5–61° (petroleum ether-ether) (Ref. 5, m.p. 61–63°) identified by comparison of the IR-spectrum with that of an authentic sample.⁶

c. 1,1,5-Trimethyl-2-formyl-4-((E)-3-acetoxy-methyl-2-butenyloxy)-cyclohexadiene-(2,5) (II). The spectroscopic data were identical with those, earlier obtained for (II).¹ $[\alpha]_D^{20} +37^\circ$ (c 1.2, CCl₄).

d. 1,1,5-Trimethyl-2-formyl-6-((E)-3-acetoxy-methyl-2-butenyloxy)-cyclohexadiene-(2,4) (IV). The spectroscopic data were identical with those, earlier obtained for (IV).¹ $[\alpha]_D^{20} +103^\circ$ (c 1.2, CCl₄).

e. A mixture of 8(*S*)-*O*-senecioid-8,9-dihydrooroseol (XIII) and 8(*S*)-*O*-isovaleryl-8,9-dihydrooroseol (XIV). The coumarins were identified by comparison of the ¹H NMR-spectrum of the mixture with those of authentic samples of (XIII) and (XIV).⁴ $[\alpha]_D^{20} +307^\circ$ (c 0.3, CH₃OH) (Ref. 4, $[\alpha]_D^{20} +303^\circ$ (c 0.3, CH₃OH) and $+305^\circ$ (c 0.4, CH₃OH) for (XIII) and (XIV), respectively).

f. 8(*S*)-*O*-Acetyl-8,9-dihydrooroseol (VIII), m.p. 134.5–135.5° (methylene chloride-petroleum ether) (Ref. 4, m.p. 135–136°). $[\alpha]_D^{20} +263^\circ$ (c 0.4, CH₃OH). ($[\alpha]_D^{20} +259^\circ$ (c 0.4, CH₃OH) for a synthetic sample). The ¹H NMR- and IR-spectra were identical with those of a synthetic sample.⁴

g. 8(*S*),9(*R*)-9-Acetoxy-*O*-isovaleryl-8,9-dihydrooroseol (X), m.p. 86.5–87° (petroleum ether-ether), $[\alpha]_D^{20} +48.1^\circ$ (c 0.6, CH₃OH) (Ref. 4, m.p. 88–88.5°, $[\alpha]_D^{20} +49^\circ$ (c 0.6, CH₃OH)). The ¹H NMR- and IR-spectra were in accordance with those of an authentic sample.⁴

h. 8(*S*),9(*R*)-9-Acetoxy-*O*-senecioid-8,9-dihydrooroseol (XI), m.p. 123–124° (methylene chloride-petroleum ether), $[\alpha]_D^{20} -44.2^\circ$ (c 1.3, CHCl₃) (Ref. 4, m.p. 126–126.5°, $[\alpha]_D^{20} -48^\circ$ (c 1.2, CHCl₃)). The ¹H NMR- and IR-spectra

were identical with those of an authentic sample.⁴

i. *1,1,5-Trimethyl-2-formyl-4-((E)-3-hydroxymethyl-2-butenyloxy)-cyclohexadiene-(2,5)* (III). A viscous liquid. $[\alpha]_{\text{D}}^{20} + 44^\circ$ (c 1.0, CCl_4). UV: λ_{max} (EtOH) 227 nm (4.43). IR: 3430 (OH), 2715, 1710 (CHO), and 1650 cm^{-1} (C=C). The ^1H NMR-spectrum was in accordance with the data given by Bohlmann and Grenz.³ Mass spectrum (sample temp. 43°): 264 (M^+ , 2), 249 (7), 231 (0.8), 203 (1.5), 167 (5), 166 (44), 151 (12), 133 (6), 121 (18), 105 (17), 100 (6), 99 (100), 91 (9), 79 (7), 77 (9), 71 (36), 53 (5), 43 (35), 41 (12), 39 (8).

(III) was separated from (V) by chromatography on 100-fold amounts of silica gel,¹ using benzene, to which ethyl acetate (10–20 %) was added, as eluent.

j. *1,1,5-Trimethyl-2-formyl-6-((E)-3-hydroxymethyl-2-butenyloxy)-cyclohexadiene-(2,4)* (V). A viscous liquid. $[\alpha]_{\text{D}}^{20} + 126^\circ$ (c 1.2, CCl_4). UV: λ_{max} (EtOH) 219 nm (4.18) and 303 nm (4.02). IR: 3420 (OH), 2710, 1700 (CHO), and 1570 cm^{-1} (conj. C=C). ^1H NMR-data (δ -values): A singlet at 9.42 is assigned to the aldehyde proton a, doublets at 6.61 (1H) ($J_{b,c} = 6$ cps), 1.95 (3H), ($J_{c,d} = \text{ca. } 1$ cps), and a multiplet at 6.08 to the protons b, d, and c, respectively, a singlet at 5.17 (1H) to the proton e, two singlets at 1.21 and 1.14 (3H each) to the gem-dimethyl protons f. The acido moiety of (V) gives rise to a multiplet at 5.90 (1H) and a doublet (3H) at 2.09 ($J_{i,j} = 1$ cps), assigned to the protons i and l, respectively, a slightly broadened singlet (2H) at 4.03, assigned to the protons j, and a broad signal (1H) at 2.5, assigned to the proton k. Mass spectrum (sample temp. 45°): 264 (M^+ , 9), 249 (2), 235 (3), 166 (20), 151 (5), 137 (12), 133 (5), 121 (13), 120 (5), 119 (8), 105 (16), 100 (7), 99 (100), 97 (6), 91 (9), 83 (45), 79 (8), 77 (9), 71 (39), 69 (5), 55 (12), 53 (7), 44 (6), 43 (43), 41 (19), 39 (13).

k. *Ostruthin* (XII), m.p. $114-116^\circ$ (aq. methanol) (Ref. 7, m.p. $117-118^\circ$). The ^1H NMR-spectrum was in accordance with that published by Nikonov *et al.*⁷

Treatment of (I) with sulfuric acid. A solution of (I) (171 mg) in a mixture of methanol (3 ml) and 4 N sulfuric acid (0.2 ml) was kept at 50° for 10 min. The reaction mixture was diluted with water (3 ml) and extracted with methylene chloride. The methylene chloride phase, which by ^1H NMR-spectroscopy was shown to contain mainly 3-methyl-2-butenic acid and 2,3,4-trimethylbenzaldehyde, was extracted with sodium hydrogen carbonate

solution. From the sodium hydrogen carbonate phase the *p*-phenylphenacyl ester of the acido moiety was prepared in the usual manner. *p*-Phenylphenacyl senecioate, m.p. $143-144^\circ$ (ethanol) was obtained. (Ref. 6, m.p. $143.5-145^\circ$). The IR-spectrum was identical with that of an authentic sample.

Treatment of (III) with sulfuric acid. The procedure previously described for (IV)¹ was used. Besides 2,3,4-trimethylbenzaldehyde (identified by TLC (tetrachloromethane-methylene chloride-ethyl acetate (2:1:1))), (*E*)-3-hydroxymethyl-2-butenic acid was isolated. Recrystallized from petroleum ether-ethyl acetate, m.p. $109.5-110.5^\circ$. (Ref. 1, m.p. $110.5-111^\circ$). The IR-spectrum was identical with that of an authentic sample.

Treatment of (V) with sulfuric acid. Using the procedure previously described for (III),¹ (V) yielded 2,3,4-trimethylbenzaldehyde and (*E*)-3-hydroxymethyl-2-butenic acid. Both compounds were identified by TLC, using tetrachloromethane-methylene chloride-ethyl acetate (2:1:1) and benzene-ethyl acetate (1:1) with 1 % of formic acid, respectively, as eluents.

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