



*Selinum carvifolium* L.<sup>1</sup> 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-dihydrooroselel (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-

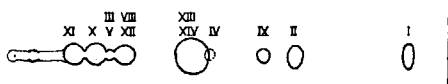


Fig. 1. Thin-layer chromatogram of the root extract. Silica gel GF<sub>254</sub> (Merck), petroleum ether-ether (2:1), 3-fold development. Visualization: long wave and short wave UV-light and spraying with 2,4-dinitrophenylhydrazine reagent.

8,9-dihydrooroselel (X), 8(*S*),9(*R*)-9-acetoxy-*O*-senecioid-8,9-dihydrooroselel (XI), and ostruthin (spot XII, Fig. 1) were isolated. Furthermore, a mixture of the senecioate and the isovalerate of 8(*S*)-8,9-dihydrooroselel, (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.<sup>1</sup> 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,<sup>1</sup> using mainly petroleum ether, to which ether or ethyl acetate was added, as eluents. The coumarins were isolated by chromatography on silica gel,<sup>1</sup> using mainly the same eluents as described in a previous paper.<sup>4</sup> 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, CCl<sub>4</sub>). UV:  $\lambda_{max}$ (EtOH) 227 nm (4.42). IR: 2715, 1710 (CHO), and 1645 cm<sup>-1</sup> (C=C). <sup>1</sup>H NMR-data ( $\delta$ -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<sup>+</sup>, 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.<sup>6</sup>

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).<sup>1</sup>  $[\alpha]_D^{20} +37^\circ$  (c 1.2, CCl<sub>4</sub>).

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).<sup>1</sup>  $[\alpha]_D^{20} +103^\circ$  (c 1.2, CCl<sub>4</sub>).

e. A mixture of 8(*S*)-*O*-senecioid-8,9-dihydrooroselel (XIII) and 8(*S*)-*O*-isovaleryl-8,9-dihydrooroselel (XIV). The coumarins were identified by comparison of the <sup>1</sup>H NMR-spectrum of the mixture with those of authentic samples of (XIII) and (XIV).<sup>4</sup>  $[\alpha]_D^{20} +307^\circ$  (c 0.3, CH<sub>3</sub>OH) (Ref. 4,  $[\alpha]_D^{20} +303^\circ$  (c 0.3, CH<sub>3</sub>OH) and  $+305^\circ$  (c 0.4, CH<sub>3</sub>OH) for (XIII) and (XIV), respectively).

f. 8(*S*)-*O*-Acetyl-8,9-dihydrooroselel (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, CH<sub>3</sub>OH). ( $[\alpha]_D^{20} +259^\circ$  (c 0.4, CH<sub>3</sub>OH) for a synthetic sample). The <sup>1</sup>H NMR- and IR-spectra were identical with those of a synthetic sample.<sup>4</sup>

g. 8(*S*),9(*R*)-9-Acetoxy-*O*-isovaleryl-8,9-dihydrooroselel (X), m.p. 86.5–87° (petroleum ether-ether),  $[\alpha]_D^{20} +48.1^\circ$  (c 0.6, CH<sub>3</sub>OH) (Ref. 4, m.p. 88–88.5°,  $[\alpha]_D^{20} +49^\circ$  (c 0.6, CH<sub>3</sub>OH)). The <sup>1</sup>H NMR- and IR-spectra were in accordance with those of an authentic sample.<sup>4</sup>

h. 8(*S*),9(*R*)-9-Acetoxy-*O*-senecioid-8,9-dihydrooroselel (XI), m.p. 123–124° (methylene chloride-petroleum ether),  $[\alpha]_D^{20} -44.2^\circ$  (c 1.3, CHCl<sub>3</sub>) (Ref. 4, m.p. 126–126.5°,  $[\alpha]_D^{20} -48^\circ$  (c 1.2, CHCl<sub>3</sub>)). The <sup>1</sup>H NMR- and IR-spectra

were identical with those of an authentic sample.<sup>4</sup>

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,  $\text{CCl}_4$ ). UV:  $\lambda_{\text{max}}$ (EtOH) 227 nm (4.43). IR: 3430 (OH), 2715, 1710 (CHO), and 1650  $\text{cm}^{-1}$  (C=C). The  $^1\text{H}$  NMR-spectrum was in accordance with the data given by Bohlmann and Grenz.<sup>3</sup> Mass spectrum (sample temp. 43°): 264 ( $\text{M}^+$ , 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,<sup>1</sup> 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,  $\text{CCl}_4$ ). UV:  $\lambda_{\text{max}}$ (EtOH) 219 nm (4.18) and 303 nm (4.02). IR: 3420 (OH), 2710, 1700 (CHO), and 1570  $\text{cm}^{-1}$  (conj. C=C).  $^1\text{H}$  NMR-data ( $\delta$ -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), ( $J_{c,d}=ca. 1$  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 ( $J_{i,l}=1$  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 ( $\text{M}^+$ , 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° (aq. methanol) (Ref. 7, m.p. 117–118°). The  $^1\text{H}$  NMR-spectrum was in accordance with that published by Nikonov *et al.*<sup>7</sup>

*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  $^1\text{H}$  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° (ethanol) was obtained. (Ref. 6, m.p. 143.5–145°). The IR-spectrum was identical with that of an authentic sample.

*Treatment of (III) with sulfuric acid.* The procedure previously described for (IV)<sup>1</sup> 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°. (Ref. 1, m.p. 110.5–111°). The IR-spectrum was identical with that of an authentic sample.

*Treatment of (V) with sulfuric acid.* Using the procedure previously described for (III),<sup>1</sup> (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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