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# Constituents of Umbelliferous Plants

## VI.* The Structure of Peulustrin, a New Coumarin from *Peucedanum palustre* L.

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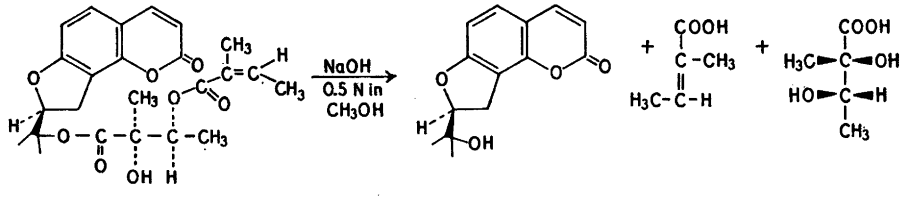
A coumarin, $C_{24}H_{28}O_8$, obtained from the root of *Peucedanum palustre* is shown to be 8(*S*)-(+)-8-(1-(2(*R*),3(*S*)-3-angeloyloxy-2-hydroxy-2-methylbutyryloxy)-1-methylethyl)-8,9-dihydro-2H-furo-[2,3-*h*]-1-benzopyran-2-one(I).

In a previous paper[1] an investigation of a crystalline coumarin fraction obtained from the ether extract of the root of *Peucedanum palustre* has been reported.

The non-crystalline fraction has now been examined. In addition to the coumarins previously found in the crystalline fraction a new coumarin, $C_{24}H_{28}O_8$, for which we propose the name *peulustrin* (I) has been isolated. From thin layer chromatographic analysis, the fraction appears to contain other fluorescent compounds. So far, none of these minor constituents have been obtained in a crystalline state.




I II III IV

This paper presents the elucidation of the structure of peulustrin (I).

The coumarin character of (I) was indicated by the blue fluorescence, by its UV-absorption: $\lambda_{max}$ 208 m$\mu$ (4.60), 217 m$\mu$ (4.38) (shoulder), 250 m$\mu$

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(3.87), 261 mμ (3.87), and 326 mμ (4.19). $\lambda_{min}$ 245 mμ (3.86), 255 mμ (3.83), and 267 mμ (3.17)and by the absorption bands in the infrared at 1715—1745, 1627, 1584, 1495, and 1458 cm.$^{-1}$ Furthermore, bands corresponding to a hydroxyl group appears in the IR-spectrum.

Treatment of (I) with 0.5 N methanolic sodium hydroxide afforded 8(*S*)-(+)-dihydro-oreselol (II), angelic acid (III), and a dihydroxy acid. From a comparison of the dihydroxy acid with an authentic sample of (+)-*threo*-2,3-dihydroxy-2-methylbutyric acid * it is evident, that the isolated acid is (+)-*threo*-2,3-dihydroxy-2-methylbutyric acid (IV), which according to Christensen and Kjær [2] has the configuration 2(*R*), 3(*S*).

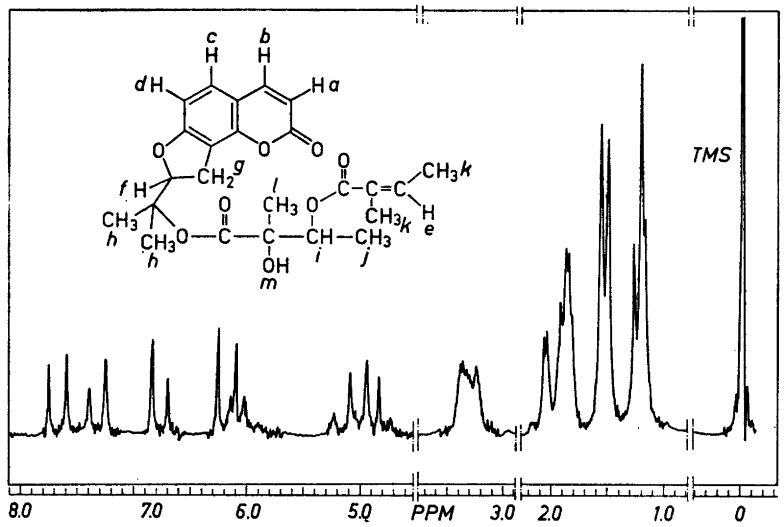


*Fig. 1.* PMR-spectrum of peulustrin (I) (deuterochloroform). Internal standard, tetramethylsilane (TMS).

The PMR-spectrum of (I) is shown in Fig. 1. The doublets at $\delta$ 6.2 and 7.7 ($J$ = 9.5 cps) are assigned to the protons labelled *a* and *b*.[3] The positions of the other pair of doublets at $\delta$ 7.3 and 6.75 ($J$ = 8 cps) are the signals from the *ortho* protons, *c* and *d*, in the benzene ring. The very broad pattern at $\delta$ 6.0 is assigned to the proton labelled *e* in angelic acid.

The pattern at $\delta$ 5, corresponding to two protons is assigned to the two CH groups labelled *f* (triplet, $J$ = 8 cps) and *i* (quartet, $J$ = 6 cps).

The pattern at $\delta$ 3.3 corresponding to three protons is assigned to the proton in the hydroxyl group (*m*) and a doublet ($J$ = 8 cps) arising from the $CH_2$-group labelled *g*.

The six proton pattern at $\delta$ 2 is assigned to the two methyl groups (*k*) in angelic acid.

* A sample of (+)-*threo*-2,3-dihydroxy-2-methylbutyric acid was kindly placed at our disposal by Professor A. Kjær, Copenhagen.

The *gem*-dimethyl protons (*h*) give rise to two singlets at $\delta$ 1.49 and $\delta$ 1.56. At $\sigma$ 1.2 is a doublet ($J$ = 6 cps) and a singlet. These signals are assigned to the methyl groups *j* and *l*, respectively.

From a comparison of the chemical shift for the proton labelled *i* in structure (I) ($\delta$ 4.9) and the chemical shift for the corresponding proton in 2,3-dihydroxy-2-methylbutyric acid methyl ester, ($\delta$ 4.0 [4]), it is evident [5] that the dihydroxy acid in the coumarin (I) is esterified with angelic acid at the secondary alcohol group. Furthermore, in the PMR-spectrum of a dimethyl sulphoxide solution of peulustrin (I), the hydroxyl group give rise to a singlet at $\delta$ 5.14, which according to Chapman and King [6] is characteristic for tertiary alcohols.

Accordingly, peulustrin is 8(*S*)-(+)-8-(1-(2(*R*),3(*S*)-3-angeloyloxy-2-hydroxy-2-methylbutyryloxy)-1-methylethyl)-8,9-dihydro-2H-furo[2,3-*h*]-1-benzopyran-2-one (I).

## EXPERIMENTAL

*Isolation of the peulustrin (I).* The diethyl ether extract of the root material (1 kg) when evaporated and left for several days in a refrigerator, deposited 28.2 g of crystals. The examination of this crystalline fraction has been presented in an earlier paper.[1]

The mother liquor (40 g) was dissolved in 90 % methanol, defatted with petroleum ether (b.p. below 50°), evaporated, and the residue (22 g) was chromatographed on silica gel (Merck, 450 g) activated at 120° and impregnated with 10 % of water. Upon elution with benzene, benzene-chloroform and subsequently chloroform-methanol the five coumarins previously isolated from the crystalline fraction were obtained. In addition, on elution with chloroform to which 40–50 % methanol had been added, a blue-fluorescent compound (0.9 g) m.p. 129.5°, (recrystallized from ether-chloroform), $[\alpha]_D^{25}$ + 278° (*c* 3.0, methanol) was eluted.

The composition was $C_{24}H_{28}O_8$. (Found: C 65.20; H 6.30; Calc.: C 64.85; H 6.35).

*Treatment with 0.5 N sodium hydroxide.* A solution of 463 mg of (I) in 10 ml of 0.5 N methanolic sodium hydroxide was kept at 50° for 1.5 h. The reaction mixture was acidified with 4 N sulphuric acid and after standing for 20 min adjusted to pH 8 with sodium carbonate solution and finally extracted with ether.

The extract, after drying and evaporation, yielded 8(*S*)-(+)-dihydro-oroselol [7] (II) which was recrystallized from methanol, m.p. 162.8–163.2°, $[\alpha]_D^{23}$ + 246° (*c* 0.9, methanol).

The aqueous phase (pH 8) was evaporated, acidified with sulphuric acid (4 N) and a volatile acid was removed by steam distillation. The distillate was neutralized, the *p*-phenylphenacyl ester prepared and chromatographed on a silicic acid column as previously described.[8] *p*-Phenylphenacyl angelate, m.p. 88.5–89.0°, was obtained. The identity was established by IR-spectroscopy.

The pH of the residue from the steam distillation was adjusted to 10 and the solution evaporated to dryness, acidified with sulphuric acid (4 N) and added to a mixture of diatomaceous earth-anhydrous sodium sulphate 3:1, (10 g). The almost dry mixture was packed into a column and eluted with diethyl ether (200 ml). The dried ether extract was evaporated and the residue converted to the *p*-phenylphenacyl ester in the usual manner.

The ester was chromatographed on silica gel (Merck, 10 g), activated at 120° and impregnated with 10 % of water. Benzene with increasing amounts of ethyl acetate was used as the eluent. With a solvent mixture containing 35 % of ethyl acetate a *p*-phenylphenacyl ester, m.p. 165° (Ref. 9, m.p. 165°), $[\alpha]_{364}^{25}$ −87° (*c* 0.3, chloroform) was obtained. Its IR-spectrum was identical with that of the *p*-phenylphenacyl ester (m.p. 164-165°, $[\alpha]_{364}^{25}$ −84° (*c* 0.2, chloroform)) of an authentic sample of (+)-*threo*-2,3-dihydroxy-2-methylbutyric acid.

Melting points, UV-, IR-, and PMR-spectra were determined as described in a previous paper.[7]

Microanalyses were performed by Dr. A. Bernhardt. Mülheim.

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