Constituents of Umbelliferous Plants

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

BENT EICHSTEDT NIELSEN and JOHN LEMMICH

The Royal Danish School of Pharmacy, Chemical Laboratory B, Copenhagen, Denmark

A coumarin, C_{24}H_{28}O_{8}, obtained from the root of *Peucedanum palustre* is shown to be 8(5)-(+-)-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.

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\text{I} \quad \begin{array}{c}
\text{II} \\
\text{III} \\
\text{IV}
\end{array}
\]

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: \(\lambda_{\text{max}}\) 208 m\(\mu\) (4.60), 217 m\(\mu\) (4.38) (shoulder), 250 m\(\mu\)


(3.87), 261 μ (3.87), and 326 μ (4.19). \( \lambda_{\text{min}} \) 245 μ (3.86), 255 μ (3.83), and 267 μ (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-oreaselol (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 has the configuration 2(R), 3(S).

![PMR spectrum](image)

*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 \( b \). 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 \(8(S)-(+)-8-(1-(2(R),3(S)-3-angeloyloxy-2-hydroxy-2-methylbutyryloxy)-1-methylethyl)-8,9-dihydro-2H-furo[2,3-b]-1-benzopyran-2-one\) (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\°C 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\°C, (recrystallized from ether-chloroform), [\(\alpha\)]\(_D^{20}\) = 278\°C (c 3.0, methanol) was eluted.

The composition was \(C_{24}H_{28}O_6\). (Found: C 65.20; H 6.30; Calc.: C 64.85; H 6.35).

*Treatment with 0.5\% sodium hydroxide.* A solution of 463 mg of (I) in 10 ml of 0.5\% methanolic sodium hydroxide was kept at 50\°C for 1.5 h. The reaction mixture was acidified with 4\% 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\((S)-(+)-dihydro-orosel\) (II) which was recrystallized from methanol, m.p. 162.8—163.2\°C, [\(\alpha\)]\(_D^{20}\) = 246\°C (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 silica acid column as previously described.\(^8\) \(p\)-Phenylphenacylangelate, m.p. 88.5—89.0\°C, 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\°C 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\°C (Ref. 9, m.p. 165\°C), [\(\alpha\)]\(_{365}^{20}\) = 87\°C (c 0.3, chloroform) was obtained. Its IR-spectrum was identical with that of the \(p\)-phenylphenacyl ester (m.p. 164-165\°C, [\(\alpha\)]\(_{364}^{20}\) = 84\°C (c 0.2, chloroform)) of an authentic sample of (+)-\(\alpha\)-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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REFERENCES
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