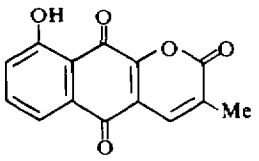
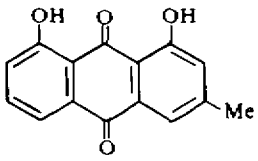


(1)



(2)

[1–3]. Comparison of the isolated compound with synthetic lambertellin [4] confirmed its identity.

A minor metabolite was also isolated by PLC and identified as chrysophanol (2) by comparison with an authentic sample.

The occurrence of lambertellin in *Lambertella* (Helotiales) and in the hyphomycete, *P. simplex*, suggests that these may be two states of a pleomorphic fungus. To date *Lambertella* species have only been known to have *Myrioconium*-like spermatial states [5, 6]. In addition to these, numerous Helotiales have pycnidial imperfect states. Only a few species have a dematiaceous hyphomycetous state, e.g. *Acrodontium* de Hoog, *Ascoconidium* Seaver, *Haplographium* Berk. & Br. and *Idriella* Nelson & Wilhelm, neither of these genera being taxonomically close to *Pseudospiropes* M. B. Ellis. On the contrary, one species of *Pseudospiropes* has a *Melanomma* perfect state (Pseudosphaeriineae). *Pseudospiropes* and *Lambertella*, therefore, probably bear no relationship to one another.

The occurrence of chrysophanol together with lambertellin is interesting in view of the biogenetic origin of the latter. Several biosynthetic routes have been suggested [3, 4, 7]; our results support Turner's hypothesis that lambertellin might arise by degradation of chrysophanol.

EXPERIMENTAL

The fungus *Pseudospiropes simplex* (Kunze ex Pers.) M. B. Ellis, CBS 674.74, was grown on 4% malt agar (Oxoid) for 25 days at 24° in daylight. Mycelium and agar were extracted with EtOAc. After evapn (101 mg from 20 petri dishes) the residue was reextracted with Et_2O. This extract was concd to a small vol. and submitted to PLC in toluene–dioxane–HOAc, 90:25:4 which gave rise to 2 yellow bands. After purification by recrystallization from $CHCl_3$–MeOH, 2:1 and Me_2CO, respectively, the band with lower R_f yielded orange plates (10 mg), mp 250°. MS *m/e* 256.0365 (M^+, 100%), calc. for $C_{14}H_8O_5$ 256.0372. This substance was seen to be identical to lambertellin by mmp, IR, UV, TLC. The second band (0.2 mg) was identified as chrysophanol by direct comparison with a purified commercial sample (UV, IR, GLC, TLC).

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(−)-3′(*R*)-HYDROXY-4′(*S*)-METHOXY-3′,4′-DIHYDROXANTHYLETIN FROM THE ROOTS OF *PEUCEDANUM ARENARIUM*

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Key Word Index—*Peucedanum arenarium*; Umbelliferae; pyranocoumarin; methyldecursidinol; (−)-3′(*R*)-hydroxy-4′(*S*)-methoxy-3′,4′-dihydroxanthyletin.

The structure of a coumarin derivative (**1**) isolated from the roots of *Peucedanum arenarium* W. et K. collected on Delibatski sands (Voevodina Serbia) is reported.

The roots of *Peucedanum arenarium* were extracted with ethanol at room temp. for 8 days. The extract was concentrated under reduced pressure. The residue, to which a little water was added, was extracted with diethyl ether. On standing, a crystalline compound (**1**) was obtained from the concentrated ether extract. Recrystallization of **1** from ethyl acetate and hexane gave colourless crystals, mp 93.5–94.5°, $[\alpha]_D^{27}$ −92.14° (*c* 0.95, MeOH). (Found: C, 65.14; H, 5.92. Calc. for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84%). MS (M^+ at *m/e* 276) established the composition of **1** as $C_{15}H_{16}O_5$. The UV and IR spectra of **1** indicated the structure was a linear dihydropyrano-

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coumarin derivative. Its UV spectrum had absorption peaks at λ_{max}^{EtOH} 220–224(*sh*), 248, 258 and 328 nm (log ε 4.22, 3.66, 3.57 and 4.27 respectively). Compound **1** had IR peaks at 1725, 1630, 1570, 1500 (coumarin CO group, C=C aromatic, α-pyrone double bond respectively) and 3430–3520 cm^{-1} (OH group).

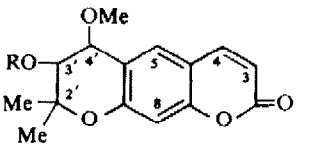
The acetylation of **1** yielded an acetate (**2**), mp 134.5 135.5°, $[\alpha]_D^{22}$ −71.17° (*c* 0.08, MeOH); $C_{17}H_{18}O_6$, (Found: C, 64.24; H, 5.88 calcd. C, 64.14; H, 5.70%) and M^+ at *m/e* 318. The UV spectrum of **2** in EtOH exhibited absorption maxima at 218–222, 246, 248 and 324 nm (log ε 4.16, 3.55, 3.37 and 4.12 respectively). Its IR spectrum showed absorption peaks at 1710–1755 cm^{-1} (CO of coumarin and of acetoxygroup).

The assignment of the signals of the NMR spectra (Table 1) of compound **1** and of its acetate **2** suggested structure **1** to be 2',2'-dimethyl-3'-hydroxy-4'-methoxy-3',4'-dihydropyrano-5',6':6,7-coumarin [1].

The chemical composition and physical and chemical properties suggest that **1** is an antipode of (+)-methyldecursidinol (3',4'-*trans*:4'*R*) on the basis of the NMR chemical shift values and the coupling constants between 3'-H and 4'-H. Our data (Table 1) for **1** and its acetate **2** agree with the results of these authors [5].

Thus compound **1** isolated from the roots of *Peucedanum arenarium* has the structure (−)-3'(*R*)-hydroxy-4'(*S*)-methoxy-3',4'-dihydroxanthyletin [(−)-methyldecursidinol (*trans*: 4'*S*)].

A number of diesters of 3'(*R*),4'(*R*)-dihydroxy-3',4'-dihydroxanthyletin have been isolated earlier from this plant, and they have been chemically transformed into **1** and **2**, but they are not totally free from the 4'(*R*)-diastereomers [6].



1 $R = -H$
2 $R = -COCH_3$

Table 1. The NMR spectra data of compound **1** and its acetate **2** ($CDCl_3$, 20°, TMS, δ)

Compound	$-C(Me)(Me)$	$-O-C(=O)-Me$	-OMe	3'-CH	4'-CH	5-H	8-H	5-H	4-H	OH
1	1.29 s, 1.48 s	-	3.56 s	3.72 *d*, 7.5 Hz	4.38 *d*, 7.5 Hz	6.25 *d*, 9.0 Hz	6.74 s	7.46 s	7.62 *d*, 9.0 Hz	3.80 br
2	1.38 s, 1.42 s	2.13 s	3.53 s	5.26 *d*, 5.0 Hz	4.31 *d*, 5.0 Hz	6.26 *d*, 9.0 Hz	6.80 s	7.46 s	7.64 *d*, 9.0 Hz	

decursidinol (lit.: $C_{15}H_{16}O_5$, mp 94–95°, $[\alpha]_D^{20}$ +92.3° and its acetate, mp 130–132°, $[\alpha]_D^{20}$ + 77). Hata *et al.* [2] have obtained this compound by separating diastereomers formed by alkaline hydrolysis of decursidin in MeOH. Both compound **1** and (+)-methyldecursidinol differ in physical constants from the product of hydrolysis of xanthalin (lit.: mp 136.5–138°, $[\alpha]_D^{20}$ −47.7°) which has the structure (−)-*trans*-3'-hydroxy-4'-methoxy-3',4'-dihydroxanthyletin suggested by Sokolova and Nikonov [3].

Sano *et al.* [4, 5] established the absolute configuration of decursidin and other pyranocoumarins. For (+)-methyldecursidinol they suggested the structure (+)-

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