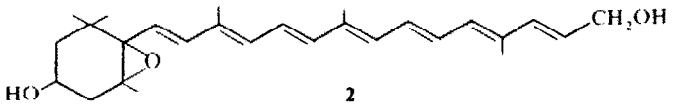
RESULTS AND DISCUSSION

The pale yellow pigment constituted *ca* 2% of the total carotenoids of the apple peel (20 μg/g fr. wt). The pigment was detected in the most polar fraction obtained from CC on MgO–Hyflo Super Cel, which is the neoxanthin fraction. Upon TLC on Si gel G the pigment was found between luteoxanthin and neoxanthin. According to its electronic spectrum and its positive epoxide test, structure **2** was proposed: 5,6-epoxy-5,6-dihydro-10′-apo-β-carotene-3,10′-diol. This structure was confirmed by MS of the pigment, its 5,8-epoxide isomer and its diacetate.

These findings provide further evidence that this new class of apocarotenols are metabolites formed only in ripe fruit. These metabolites may be formed through the Glover–Redfearn degradation of the most abundant pigment present. Thus in avocado, chrysanthemaxanthin [10] yields pigment **1**; in apple, where at this stage of maturation violaxanthin is the main pigment, it yields pigment **2**.



2

Evidence that an enzymatic reduction occurs subsequently must still be produced.

EXPERIMENTAL

The analytical methods were as reported previously [11]. Prior to extraction, a neutralizing agent was added. After extraction, saponification and removal of sterol, the extract was chromatographed on a column of MgO–Hyflo Super Cel (1:1). The column was developed stepwise with increasing amounts of Me_2CO in petrol. The most polar fraction was separated by developing with Me_2CO–petrol–EtOH (9:88:3). This neoxanthin fraction was further separated by TLC on Si gel G developed with Me_2CO–petrol (2:3). The pale yellow pigment was situated between luteoxanthin and neoxanthin. Its electronic spectrum λ_{max} 372, 394, 418 nm was indicative for a heptaene chromophore. This spectrum was identical with that of Curl's reduced violaxanthal. The HCl–epoxide test was positive, with a hypsochromic shift of 22 nm. The 5,8-furanoxide had the spectrum 353, 372, 395 nm identical with that of (**1**). For high resolution MS the samples were introduced via the probe inlet system, the source temp. varied between 200–250°, the ionizing voltage was 70 eV.

The elementary composition of **2** was $C_{27}H_{38}O_3$ (Found 410.2816; calc. 40.2821). Fragments at *m/e* 221 ($C_{14}H_{21}O_2$) and 181 ($C_{11}H_{17}O_2$) supported the presence of the 3-hydroxy-epoxide ring. Its diacetate gave the M^+ at *m/e* 494 ($C_{31}H_{42}O_5$) and the characteristic fragments for the end groups shifted to *m/e* 263 ($C_{16}H_{23}O_3$) and 223 ($C_{13}H_{19}O_3$). The 5,8-epoxide isomer (**1**) exhibited the same MS as **2**: *m/e* 410 ($C_{27}H_{38}O_3$, M^+), 330 ($[M\text{-}C_6H_8]^+$); 221 ($C_{14}H_{12}O_2$); 181 ($C_{11}H_{17}O_2$). This MS is identical with that of the pigment isolated from avocado pulp [8].

Acknowledgements—This work was supported by the Deutsche Forschungsgemeinschaft.

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LAMBERTELLIN AND CHRYSOPHANOL FROM THE IMPERFECT FUNGUS *PSEUDOSPIROPES SIMPLEX*

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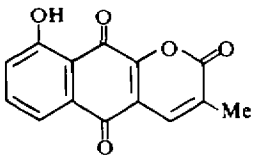
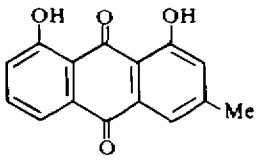
(*Received* 10 *March* 1978)

Key Word Index—*Pseudospiropes simplex*; Hyphomycetes; fungi; lambertellin; 9-hydroxy-3-methylnaphtho[2,3-b]pyran-2,5,10-trione; chrysophanol; 1,8-dihydroxy-3-methylanthraquinone.

From the EtOAc extract of 25-day-old cultures of *Pseudospiropes simplex*, an orange-red crystalline substance was isolated by PLC which became violet in aq. Na_2CO_3. Its IR spectrum showed a band at 1620 cm^{-1}, characteristic of a hydrogen-bonded quinone group, in addition to absorptions at 1742 and 1660 cm^{-1}. The compound showed the UV absorption of a juglone and formed an acetate. High resolution MS gave the molecular formula $C_{14}H_8O_5$. A compound with similar physico-chemical properties is the pyranonaphthoquinone, lambertellin (**1**), a pigment hitherto only reported from the discomycete genus *Lambertella* Höhn



(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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