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NOVEL DIHYDROSTILBENE FROM FRONDS OF *NOTHOLAENA DEALBATA* AND *NOTHOLAENA LIMITANEA*

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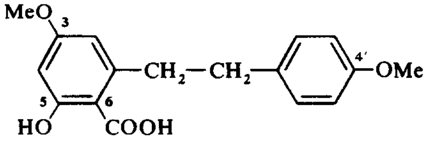
Key Word Index—*Notholaena dealbata*; *N. limitanea*; Polypodiaceae; frond exudate; dihydrostilbene; 5-hydroxy-3,4′-dimethoxy-6-carboxylic bibenzyl.

Notholaena dealbata (Pursh) Kze. and *N. limitanea* Maxon, like many other species of the genus, bear a farinose coating mainly on the under surface of their fronds. Tyron's description [1] of *N. dealbata* reads "upper surface glabrous or sparingly white-ceraceous, the lower densely white-ceraceous", and of *N. limitanea*, "upper surface glabrous or very slightly white-ceraceous, glaucous, the lower white or rarely white-yellowish ceraceous, usually densely so". From previous results with other species of the genus [2], the white farina was assumed to be composed of flavonoid aglycones—free flavones, flavonols or dihydrochalcones. However, on TLC viewed in long-wave UV light almost nothing can be seen; spraying with 'Naturstoffreagenz A' reveals some very faint spots, one of them appearing somewhat hazy. This spot, by comparison with an authentic sample, has been shown previously to be due to genkwanin [3]. Why, then, did it appear so strange? Vizualization of chromatograms in short-wave UV light (before spraying) shows for *N. dealbata*, as well as for *N. limitanea*, an important light blue spot, strongly tailing and thus concealing the faint genkwanin spot. This obviously was no flavonoid, nor was it lipoid material. Recently we obtained fronds from several plants of both species and thus were able to isolate the major components of the farinas. This substance could be shown by spectroscopic methods to be a novel dihydrostilbene. In the following we report on the elucidation of its structure.

RESULTS AND DISCUSSION

By comparison of TLC behaviour, UV spectra and mass spectra it became evident that the two substances isolated as major farina constituents of *N. dealbata* and *N. limitanea* were identical products. From the UV spectrum ($\lambda_{\max}^{\mathrm{MeOH}}$ 304, 264, 223 nm) it was assumed that the substance is a phenolic compound, probably a bibenzyl. MS showed the following fragmentation: *m/e* (rel. int.) 302 (M^+; 6%, 302.1153; calc. for $C_{17}H_{18}O_5$: 302.1154), 258 ($M^+ - CO_2$; 2%; 258.1250; calc. for $C_{16}H_{18}O_3$: 258.1255), 181 (4), 135 (15), 121 (100; 121.0657; calc. for C_8H_9O: 121.0653), 91 (121 − 30 m*; 10%). The interpretation of the ^{1}H NMR spectrum indicates that the molecule consists of one *p*-disubstituted benzene ring (δ 7.14, *d*, 2H; 6.94, *d*, 2H, $J = 8.5$ Hz) and one tetrasubstituted benzene ring (δ 6.28 and 6.36 ppm, 2H in *m*-position; $J = 2.5$ Hz). In addition, the ^{1}H NMR signals indicate the presence of two OMe groups (δ 3.80 ppm) and a —CH_2—CH_2— bond (δ 2.8 ppm, *m* and 3.20 ppm, *m*). MS and IR further point to a carboxyl group (*m/e* 258 = $M^+ - 44$; ν CO 1650 cm^{-1}). The chemical shifts of the —CH_2— groups suggest their position as a linkage between the two benzene rings thus leading to a dihydrostilbene skeleton, which is in accordance with the UV spectrum and literature data for bibenzyls [4]. Under these circumstances, one OMe can be assigned to the *p*-disubstituted benzene ring. The base peak in the MS, appearing at *m/e* 121, can be explained by the fragment —CH_2—C_6H_4—OMe; metastable transition yields *m/e* 91 for —CH_2—C_6H_5. A peak at *m/e* 181 shows the second stable portion of the original molecule. The second benzene ring thus bears the carboxyl group and one OMe group, as well as an OH group (the latter being shown by MS of the TMSi derivative). The shielding of the two protons on this ring excludes their proximity to the carboxylic acid function. Strong hydrogen-bonding of the CO to an OH group in the *o*-position leads us to suggest the structure given below. The presence of the acid function near to the CH_2 explains the relative deshielding of the latter. The presence of long distance coupling between each CH_2 and its nearest aromatic protons allows them to be assigned to the appropriate position in the ^{1}H NMR spectrum, the couplings being revealed by irradiation experiments.



The phenolic compound forming most of the farina on fronds of *N. dealbata* and *N. limitanea* is thus a dihydrostilbenic acid, or 5-OH-3,4′-diOMe-6-carboxylic bibenzyl, for which we suggest the name notholaenic acid. This substance belongs to a very rare group of natural products. So far only 4 compounds of this type have been found in nature, namely dihydropinosylvin monomethyl ether from various *Pinus* species, lunularic acid (dihydrohydrangeic acid) and pellepiphyllin from some liverworts (*Lunularia*, *Marchantia*, *Pellia*, etc.) and 3,4′-diOH-4,5-diOMe bibenzyl from the heartwood of *Combretum molle* (cited in [5]). The dihydrostilbene, described here for the first time, occurring in the farina of two gymnogrammoid ferns, seems to be excreted also by a few other species of *Notholaena*. Its distribution possibly indicates taxonomic relations, as assumed for those representatives of the genus which exude esterified flavonols [6]. These relations will be studied further.

EXPERIMENTAL

Plants of *N. dealbata* were collected in Texas (Travis Co.; D. Seigler Nos. 1033 and 1035), *N. limitanea* was collected in Arizona (Cochise Co.; D. Seigler No. 2351). Dried fronds were rinsed with Me_2CO to dissolve the exudate material and the soln evapd to dryness. Fronds of *N. dealbata* (12.5 g) yielded 0.596 g of crude extract (4% dry wt); fronds of *N. limitanea* (4.67 g) yielded 0.158 g of crude extract (3.4% dry wt). This material was crystallized ×3 from MeOH, then twice from C_6H_6. In both cases the major component of the farina was obtained as colourless fine needles, mp 148–149° (*N. dealbata*, *ca* 250 mg) and 149–150° (*N. limitanea*, *ca* 100 mg), respectively. The solvent used for TLC on polyamide DC-11 was toluene–petrol (100–140°)–MeCOEt–MeOH, 12:6:2:1 (corresponding to E.W.'s former standard solvent 60:26:7:7 [7]. C_6H_6 has been replaced by toluene, which in some solvent mixtures requires slight alterations in proportions). The plates were viewed in UV light before and after spraying with 'Naturstoffreagenz A' (β-aminoethyl ester of diphenyl boric acid). MS were measured at 70 eV at the Institute of Organic Chemistry of the TH Darmstadt. ^1H NMR spectra were recorded in MeOH-d_4 at 100 MHz at the Université Cl. Bernard Lyon I.

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REFERENCES

1. Tryon, R. (1956) *Contrib. Gray Herb. Harv. Univ.* **179**, 1.
2. Wollenweber, E. (1978) *Am. Fern. J.* **68**, 13.
3. Wollenweber, E. (1976) *Ber. Dtsch. Bot. Ges.* **89**, 243.
4. Letcher, R. M., Nhamo, L. R. M. and Gumiro, I. T. (1972) *J. Chem. Soc.* 206.
5. Devon, T. K. and Scott, A. I. (1975) *Handbook of Naturally Occurring Compounds*, Vol. I. Acacemic Press, New York.
6. Wollenweber, E., Favre-Bonvin, J. and Jay, M. (1978) *Z. Naturforsch. Teil C* 33, 831.
7. Wollenweber, E. (1976) *Phytochemistry* **15**, 438.

NOTE ADDED IN PROOF

Three further bibenzyls had been described previously: 3-OMe-bibenzyl from *Radula complanata* (see Asakawa, Y., Kusube, E., Takemoto, T. and Suire, C. (1978) *Phytochemistry* 17, 2115), 3,4,5,3′,4′,5′-hexaOMe-bibenzyl (brittonin A) from *Frullania brittoniae* subsp. *truncatifolia* (Asakawa, Y., Tanikawa, K. and Aratoni, T. (1976) *Phytochemistry* **15**, 1057) (both liverworts), and 3,3′-diOH-5-OMe-bibenzyl from yam bulbils, *Dioscorea batatas* (Hashimoto, T. and Hasegawa, H. (1974) *Phytochemistry* **13**, 2849).

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8-HYDROXYCAPILLARIN—EIN NEUES ISOCUMARIN AUS *ARTEMISIA DRACUNCULUS*

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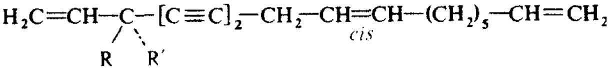
Key Word Index—*Artemisia dracunculus*; Compositae; Anthemideae; root acetylenes; 8-hydroxycapillarin.

Im Rahmen vergleichender Untersuchungen über aromatische Polyine und Dehydrofalcarinon-Derivate in der *Artemisia dracunculus*-Gruppe wurden die Wurzel-Acetylene einer decaploiden Gartenherkunft von *Artemisia dracunculus* L. isoliert und aufgeklärt. Neben Dehydrofalcarinon (**1**) und Dehydrofalcarinol (**2**) wurde hier in Übereinstimmung mit früheren Befunden [1] Capillen (**3**) und in hoher Konzentration Capillarin (**4**) festgestellt. Außerdem wurde ein Derivat des Capillarins isoliert, das bisher noch nicht bekannt war.

Die massenspektroskopisch ermittelte Summenformel $C_{13}H_{10}O_3$ deutet bereits an, daß die Verbindung eine zusätzliche OH-Gruppe besitzt. Entsprechend erkennt man im ^1H-NMR-Spektrum ein tiefliegendes Singulett bei 10.03 für eine wasserstoffbrückengebundene OH-Gruppe, die demnach nur an C-8 stehen kann. Die Aromatensignale zeigen, daß die Verbindung drei vicinale Wasserstoffe besitzt [*dd* 6.88 (J = 7.5, 1.0), *dd* 7.59 (J = 8, 7.5), *dd* 6.95 (J = 8, 0.7)]. Die gegenüber Capillarin unveränderten Signale der Seitenkette zeigen, daß nur die Konstitution (**5**) für den neuen Naturstoff in Betracht kommt.

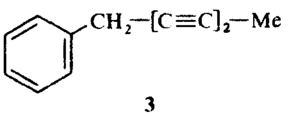
Im Gegensatz zu einer kürzlich untersuchten, octoploiden *A. dracunculus* aus Taschkent [2] konnten hier keine Buten-(1)-yl-isocumarine nachgewiesen werden.



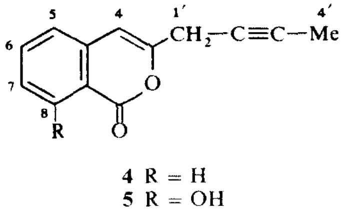
$$H_2C{=}CH{-}\underset{R\ \ R'}{C}{-}[C{\equiv}C]_2{-}CH_2{-}\underset{cis}{CH{=}CH}{-}(CH_2)_5{-}CH{=}CH_2$$

1 $\left.\begin{matrix}R\\R'\end{matrix}\right\} = O$

2 $R = OH$, $R' = H$



3



4 R = H
5 R = OH