ERIODERMIN, A DICHLORODEPSIDONE FROM THE LICHEN ERIODERMA PHYSCIOIDES—CRYSTAL STRUCTURE ANALYSIS*

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Abstract—The structure of eriodermin, a depsidone from the lichen *Erioderma physcioides*, has been established as 4-formyl-2,7-dichloro-3-hydroxy-8-methoxy-1,6-dimethyldi-benzo[b,e][1,4]dioxepin-11-one by X-ray analysis.

INTRODUCTION

In the course of the chemical analysis of numerous lichens collected by one of us (K.K.) in Brazil, we isolated from *Erioderma physcioides* Vain. a new compound which we named eriodermin.

RESULTS AND DISCUSSION

Eriodermin (1) crystallized from acetone in prisms of mp 234-236° (modification A) and from chloroform-ethanol in silk-like needles of mp 233-234°

(modification B). Both modifications were completely identical in the IR, NMR and mass spectra. Eriodermin had, according to the high resolution mass spectrum, the formula C₁₇H₁₂Cl₂O₆ (found 382.0009; calc. 382.0011) and its UV spectrum with $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 234 (4.18) and S 254 (4.06) was typical for a depsidone. The ¹H NMR spectrum (200 MHz, CDCl₃) of 1 showed signals at δ 2.45 3H, s, Me), 2.56 (3H, s, Me), 3.86 (3H, s, OMe), 6.73 (1H, s, aromatic H), 10.68 (1H, s, CHO) and 12.80 (1H, s, OH). To determine the sequence of the substituents on the aromatic rings an X-ray crystal structure analysis of 1 (modification A) was undertaken and led to the struc-4-formyl-2,7-dichloro-3-hydroxy-8-methoxy-1,6dimethyldibenzo[b, e][1,4]dioxepin-11-one. Figure 1 shows an ORTEP diagram of eriodermin with bond distances. The dihedral angle between the planes of the

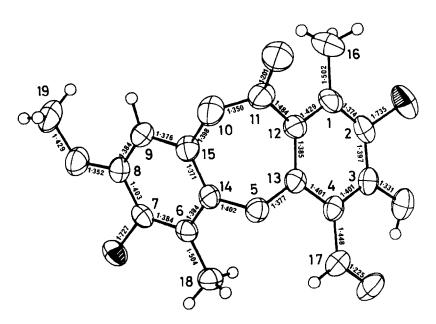


Fig. 1. ORTEP drawing of eriodermin.

^{*}Part 141 in the series "Lichen Substances". For Part 140 see Huneck, S. (1984) Phytochemistry 23, 431.

1 R=H,R'=CHO 2 R=Ac,R'=CH(OAc)₂

two benzene rings is 65°. The oxygen-oxygen separation in the intramolecular hydrogen bond between the phenolic hydroxyl and the formyl group is 2.57 A. Details of the molecular parameters are deposited at the Cambridge Crystallographic Data Centre.

On treatment with $Ac_2O-H_2SO_4$ eriodermin afforded the triacetate 2, mp 221-223° with ¹H NMR signals (200 MHz, CDCl₃) at δ 2.09 (6H, s, 2 × Me), 2.39 (3H, s, Me), 2.40 (3H, s, Me), 2.53 (3H, s, Me), 3.85 (3H, s, OMe), 6.70 (1H, s, aromatic H) and 8.30 (1H, s, -CH(OAc)₂). Alkaline hydrolysis of eriodermin yielded the diphenyl ether carboxylic acid 3.

Galloway and Jørgensen [1] found in Erioderma physcioides and in E. sorediatum D. Gall. et P. M. Jørg. a para-phenylenediamine-positive substance similar to pannarine in its R_f value. This compound was also reported from E. pedicellatum (Hue) P. M. Jørg. (= E. boreale Ahln.) [2] and is very probably identical with eriodermin.

EXPERIMENTAL

Eriodermin (1). Air dried and pulverized Erioderma physcioides (14 g, Brazil, Sao Paulo, Praia de Peruibe near Itanhaém; leg. M. Marcelli et K. Kalb, det. A. Henssen; voucher specimens will be distributed by K. Kalb in his collection Lichenes neotropici) was extracted with Et₂O (100 ml) and the extract concd to a vol. of 10 ml. The crude eriodermin (0.41 g, 2.9%) was removed by filtration, dissolved in C_6H_6 and chromatographed on silica gel (5 g). C_6H_6 (300 ml) eluted eriodermin which crystallized from Me_2CO in prisms of mp 234–236° and had R_f s 0.52 (Merck silica gel PF 254 + 366, n-hexane–Et₂O–HCO₂H, 15:10:3, UV) and

0.41 (Kodak 6061 silica gel, cyclohexane—CHCl₃—MeCOEt, 1:1:1, p-phenylenediamine \rightarrow orange spot). It gave an orange colour with p-phenylenediamine (in EtOH) and a red-brown colour with FeCl₃ (in EtOH). IR $\nu_{\rm max}^{\rm KBr}$ cm⁻¹: 722, 738, 800, 828, 874, 906, 954, 1010, 1054, 1082, 1098, 1142, 1206, 1256, 1296, 1354, 1382, 1440, 1472, 1556, 1580, 1640, 1712, 2950, 3500. UV $\lambda_{\rm max}^{\rm MeOH+NaOH}$ nm (log ε): 222 (4.15), 262 (4.15), 306 (3.98), 370 (3.56). ¹³C NMR (50.3 MHz, CDCl₃): C-1: δ 161.2, C-2: 110.8, C-3: 161.2, C-4: 119.9, C-6: 153.5, C-7: 121.3, C-8: 150.7, C-9: 102.4, C-11: 163.0, C-12: 114.0, C-13: 130.0, C-14: 142.8, C-15: 142.6, C-16: 19.9, C-17: 192.6, C-18: 14.4, C-19: 56.6. MS m/z (rel. int.): 386 (13), 384 (75), 382 (100) [M]⁺, 371 (6), 369 (21), 367 (32) [M - Me]⁺, 349 (82), 347.0320 (98) [M - Cl]⁺; calc. for C₁₇H₁₂ClO₆ 347.0323. 319 (60), 260 (60), 233 (98), 198 (43), 170.0137 (62); calc. for C₈H₇ClO₂ 170.0135.

Triacetyleriodermin (2). Eriodermin (0.1 g) was treated with $Ac_2O-H_2SO_4$ (3 ml of a mixture of 5 ml Ac_2O and one drop of conc. H_2SO_4) at room temp. for 24 hr. After the usual work up and crystallization from CHCl₃-MeOH, 2 was obtained as prisms of mp 221-223°. $C_{23}H_{20}Cl_2O_{10}$ (527.3). IR v_{max}^{KBr} cm⁻¹: 694, 716, 750, 842, 864, 886, 896, 950, 992, 1010, 1080, 1100, 1146, 1190, 1210, 1230, 1270, 1350, 1370, 1432, 1472, 1560, 1582, 1760, 1080.

Alkaline hydrolysis of eriodermin. A soln of 1 (0.1 g) in KOH (5 ml, 10%) was heated on a waterbath for 2 hr. After cooling the soln was acidified with $\rm H_2SO_4$ (10%) and the ppt filtered, washed with $\rm H_2O$, dried and crystallized from MeOH to yield 2-carboxy-3,6'-dimethyl-4,5'-dichloro-5,2'-dihydroxy-6-formyl-4'-methoxy-diphenyl ether (3) in yellowish prisms of mp 212-214°. $\rm C_{17}H_{14}Cl_2O_7$ (401.2). IR $\rm v^{KBr}_{max}$ cm⁻¹: 840, 910, 954, 990, 1030, 1090, 1110, 1170, 1190, 1236, 1290, 1344, 1390, 1442, 1486, 1562, 1604, 1640, 1698, 3000, 3500.

Crystal data. Space group P_{2_1}/c , Z=4, V=1622 A^3 , $C_{calc}=1.57$ g/ml, a=15.805, b=13.956, c=7.372 A, $\beta=95.14^\circ$. A single crystal was mounted on an Enraf-Nonius CAD-4 automatic diffractometer using Mo K_{α} ($\lambda=0.7107$ A) radiation and 3763 reflections collected. All the reflection data were used to solve the structure by routine application of MITHRIL [Gilmour, C. J., private communication]. Least-squares refinement on 2746 independent reflections $I \ge 2.5$ δ_I gave a final R-value of 0.038 ($R_{\omega}=0.06$). All hydrogen parameters and their isotropic thermal parameters were included in the final least-squares calculation.

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