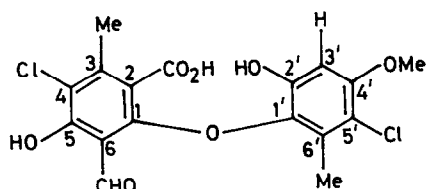


1 R = H, R' = CHO

2 R = Ac, R' = CH(OAc)₂



3

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 Å. Details of the molecular parameters are deposited at the Cambridge Crystallographic Data Centre.

On treatment with Ac₂O–H₂SO₄ 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 parranine 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 C₆H₆ and chromatographed on silica gel (5 g), C₆H₆ (300 ml) eluted eriodermin which crystallized from Me₂CO in prisms of mp 234–236° and had R_fs 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 → orange spot). It gave an orange colour with *p*-phenylenediamine (in EtOH) and a red–brown colour with FeCl₃ (in EtOH). IR $\nu_{\text{max}}^{\text{KBr}}$ 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 $\lambda_{\text{max}}^{\text{MeOH}+\text{NaOH}}$ 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 Ac₂O–H₂SO₄ (3 ml of a mixture of 5 ml Ac₂O and one drop of conc. H₂SO₄) 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°. C₂₃H₂₀Cl₂O₁₀ (527.3). IR $\nu_{\text{max}}^{\text{KBr}}$ 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, 2950.

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 H₂SO₄ (10%) and the ppt filtered, washed with H₂O, dried and crystallized from MeOH to yield 2-carboxy-3,6-dimethyl-4,5'-dichloro-5,2'-dihydroxy-6-formyl-4'-methoxydiphenyl ether (**3**) in yellowish prisms of mp 212–214°. C₁₇H₁₄Cl₂O₇ (401.2). IR $\nu_{\text{max}}^{\text{KBr}}$ 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 P₂₁/c, Z = 4, V = 1622 Å³, C_{calc} = 1.57 g/ml, a = 15.805, b = 13.956, c = 7.372 Å, β = 95.14°. A single crystal was mounted on an Enraf–Nonius CAD-4 automatic diffractometer using Mo K_α (λ = 0.7107 Å) 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 ≥ 2.5 δ_I gave a final R-value of 0.038 (R_w = 0.06). All hydrogen parameters and their isotropic thermal parameters were included in the final least-squares calculation.

Acknowledgement—We thank Dr. P. Franke, Institute of Molecular Biology, Berlin, for measuring the high resolution MS of eriodermin, Prof. Dr. A. Henssen, University of Marburg, for determining *E. physcioides* and Dr. A. Preiss, Institute of Plant Biochemistry, Halle, for recording the NMR spectra.

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