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PSEUDOCYPHELLARINS A AND B, TWO FULLY SUBSTITUTED DEPSIDES FROM THE LICHEN *PSEUDOCYPHELLARIA ENDOCHRYSEA**†

SIEGFRIED HUNECK

Institute of Plant Biochemistry, Research Centre for Molecular Biology and Medicine of the Academy of Sciences of the G.D.R., 401 Halle/Saale, Weinberg, German Democratic Republic

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Key Word Index—*Pseudocyphellaria endochrysea*; Stictaceae; lichen; pseudocyphellarin A; pseudocyphellarin B; depsides.

Abstract—The structures of two fully substituted depsides, pseudocyphellarins A and B, have been elucidated by spectroscopic and chemical methods from the lichen *Pseudocyphellaria endochrysea*.

INTRODUCTION

In the course of our chemical investigations of Antarctic lichens [1] we isolated from *Pseudocyphellaria endochrysea* two new compunds, pseudocyphellarin A and pseudocyphellarin B. The structural elucidation of both substances is described in the present paper.

RESULTS AND DISCUSSION

Pseudocyphellarin A, mp 173–175°, has according to the high resolution mass spectrum the formula $C_{21}H_{22}O_8$ (found *m/z* 402.1306; calculated 402.1315) and a UV spectrum with λ_{max}^{MeOH} (log ε) 218 (4.15), 250 (4.36), S 270 (4.21), S 290 (3.96) and 342 nm (3.30) and $\lambda_{max}^{MeOH+NaOH}$ (log ε) 221 (4.29), 286 (4.19) and S 302 (4.13) similar to the UV spectrum of nephroarctin with λ_{max}^{MeOH} (log ε) 238 (3.81), S 259 (3.97), 281 (4.09), 315 (4.00) and 379 nm (3.54) [2]. Pseudocyphellarin A gave a yellow colour with *p*-phenylenediamine, indicative of an aldehyde group. The ^{1}H NMR spectrum (100 MHz, $CDCl_3$) of pseudocyphellarin A showed five methyl signals at δ 2.05, 2.06, 2.15, 2.45 and 2.70, a methoxy group signal at δ 3.95, an aldehyde signal at δ 10.34 and three hydroxyl group signals at δ 11.06, 12.32 (*br*) and 13.00, proving the presence of a fully substituted depside.

To discover the disribution of the subsituents at the S- and A-parts of the depside, pseudocyphellarin A was submitted to *tert.*-butanolysis [3, 4], which gave after chromatography two main products (S and A) and a minor one (S'). Compound S, mp 117–119°, gave in the mass spectrum a $[M]^+$ peak at *m/z* 266 corresponding to the formula $C_{14}H_{18}O_5$, in the ^{1}H NMR spectrum (100 MHz, $CDCl_3$) signals at δ 1.60 (*s*, 9H, $-CMe_3$), 2.07 (*s*, 3H, –Me), 2.44 (*s*, 3H, –Me), 10.24 (*s*, 1H, –CHO), 12.44 (*br s*, 1H, –OH) and 12.70 (*s*, 1H, –OH) and proved to be *tert.*-butyl 2,4-dihydroxy-3-formyl-5,6-dimethylbenzoate (**1**). Saponification of **1** with KOH–MeOH led to 2,4-dihydroxy-3-formyl-5,6-dimethylbenzene (**2**) [5]. The minor cleavage product S' was identical with **2**. Compound A, mp 92–94°, showed in the ^{1}H NMR spectrum (100 MHz, $CDCl_3$) signals at δ 2.11 (*s*, 6H, 2 × –Me), 2.40 (*s*, 3H, –Me), 3.91 (*s*, 3H, $-CO_2Me$), 5.90 (*br s*, 1H, –OH) and 11.38 (*s*, 1H, –OH) and proved to be identical with an authentic sample of methyl 2,4-dihydroxy-3,5,6-trimethylbenzoate (**3**) (IR, mmp and R_f in three different solvent systems) [6]. Cleavage product **3** gave on hydrolysis with KOH–H_2O 2,4-dihydroxy-3,5,6-trimethylbenzene (**4**).

Hence the S- and A-parts of pseudocyphellarin A are 2,4-dihydroxy-3-formyl-5,6-dimethylbenzoic acid and 2,4-dihydroxy-3,5,6-trimethylbenzoic acid, respectively. Because in nearly all of the naturally occurring depsides the *p*-hydroxyl group of the A-part of the molecule is connected to the S-part, pseudocyphellarin A should have structure **5**. This structure was finally proved by Dr. J. A. Elix (personal communication) who synthesized compound **5** and found it to be identical with pseudocyphellarin A in all respects (^{1}H NMR, mp, mmp and TLC R_f values in several solvents). Acetylation of **5** with Ac_2O–H_2SO_4 gave the pentaacetate **6** and methylation with dimethyl sulphate–potassium carbonate in dimethyl formamide yielded the tri-*O*-methyl ether **7**. Alkaline hydrolysis of **7** gave 2,4-di-*O*-methyl-3-formyl-5,6-dimethylbenzoic acid (**8**). Hydrogenation of **5** with palladium on charcoal led to hypopseudocyphellarin A (**9**).

Pseudocyphellarin B, mp 168–169°, showed in the ^{1}H NMR spectrum (100 MHz, $CDCl_3$–DMSO-d_6) five methyl signals at δ 2.02 (*s*, 6H, 2 × –Me), 2.11, 2.35 and 2.57 (3 × *s*, 3 × 3H, 3 × –Me), a methoxy group signal at δ 3.92, a signal of a benzylic hydroxyl group at δ 4.89 (*s*, 2H, $-\underline{CH_2}OH$) and three hydroxyl group signals at δ 3.13 (*br s*, 1H, –OH), 10.33 (*br s*, 2H, 2 × –OH) and 11.33 (*s*, 1H, –OH). The mass spectrum of pseudocyphellarin B did not show a $[M]^+$ but gave peaks at *m/z* 210 and 178, corresponding to the fragment ions **a**, $C_{11}H_{14}O_4$ (found 210.0896; calculated 210.0892), and **b**, $C_{10}H_{10}O_3$ (found 178.0632; calculated 178.0630). On acetylation of

*Part 140 in the series "Lichen Substances". For Part 139 see Huneck, S. and Steglich, W. (1983) *Phytochemistry* **22**, 2855.

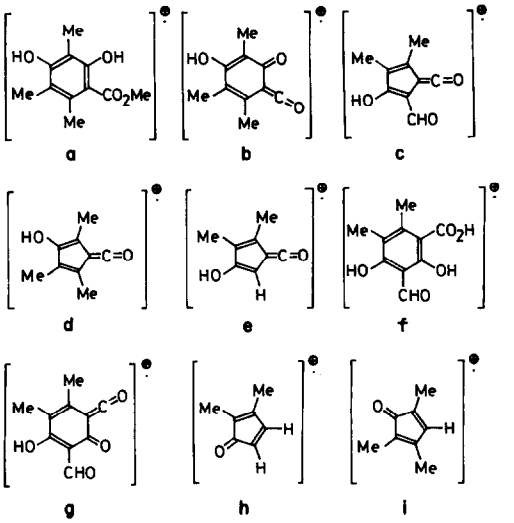
†Dedicated in friendship to Prof. Dr. Josef Poelt (Institute of Botany, University of Graz) on the occasion of his sixtieth birthday.

pseudocyphellarin B with Ac_2O–H_2SO_4 a tetraacetate, mp 145–146°, resulted, the ^1H NMR spectrum (100 MHz, $CDCl_3$) of which showed the following signals: δ 1.97, 1.99, 2.08, 2.12, 2.17 (5 × *s*, 5 × 3H, 5 × –Me), 2.23 (*br s*, 6H, 2 × –Me), 2.32 and 2.44 (2 × *s*, 2 × 3H, 2 × –Me), 3.85 (*s*, 3H, $-CO_2Me$) and 4.96 (*s*, 2H, $-CH_2-OAc$). *tert.*-Butanolysis of pseudocyphellarin B gave surprisingly 2,6-dihydroxy-3,4-dimethyl-5-*tert.*-butoxycarbonyl-1-benzyl *tert.*-butyl ether (**10**) and methyl 2,4-dihydroxy-3,5,6-trimethylbenzoate (**3**), identical in all respects with the cleavage product of pseudocyphellarin A. These results and biogenetic considerations led to structures **11** and **12** of pseudocyphellarin B and its tetraacetate, respectively.

The comparison of the chemical shifts of the methyl group signals of pseudocyphellarin A (**5**), pentaacetylpseudocyphellarin A (**6**), tri-*O*-methylpseudocyphellarin A (**7**), hypopseudocyphellarin A (**9**), pseudocyphellarin B (**11**), tetraacetylpseudocyphellarin B (**12**), nephroarctin (**13**), methyl 2,4-dihydroxy-3,5,6-trimethylbenzoate (**3**), 2,4-dihydroxy-3,5,6-trimethylbenzene (**4**) and methyl 2,4-dihydroxy-3,6-dimethylbenzoate (**14**) (Table 1) reveals an interesting phenomenon. Only in depsides with a free 2-hydroxyl group (**5**, **9**, **11** and **13**) do the chemical shifts of the methyl groups at C-5′ appear between δ 2.57 and 2.73. What is the reason for these high values? One can assume that there is a strong hydrogen bridge between the hydroxyl proton at C-2 and the depside carbonyl group. This is proved by the IR spectra of **5**, **9**, **11** and **13** with carbonyl bands at 1630 and 1640 cm^{-1}. Assuming a more or less planar conformation of the whole molecule, the methyl group either at C-3′ or C-5′ comes very close to the depside carbonyl group and is thus deshielded. In the depsides with an acetoxy or methoxy group at C-2 no hydrogen bond to the depside carbonyl group is possible and in consequence the molecule has another non-planar conformation.

The most important fragment ions of the mass spectra of **1**, **3**, **5** and **11** are shown in Scheme 1.

Besides pseudocyphellarins A and B, the following compounds were isolated from *P. endochrysea*: 3-oxostictan-22α-ol, 2α-acetoxystictan-3β,22α-diol, stictan-2α,3β,22α-triol, a mixture of polyols and a mixture of triacylglycerols with palmitic, oleic, linoleic and linolenic acids as components.



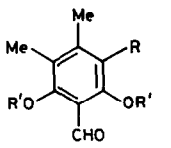
Scheme 1. Mass spectral fragmentations of compounds **1**, **3**, **5** and **11**.

EXPERIMENTAL

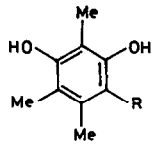
Extraction. Air-dried and pulverized *P. endochrysea* (Del.) Vain. (198.5 g; from South Georgia, Dartmouth Point, leg. et det. R. I. Lewis Smith, 2 March 1982; voucher specimen deposited at the herbarium of S.H.) was extracted with Et_2O for 20 hr, the extract freed from solvent, the residue dissolved in $CHCl_3$, adsorbed on silica gel (with 5% H_2O; 50 g) and put on the top of a column with silica gel (with 5% H_2O; 500 g) in *n*-hexane. Elution with *n*-hexane–Et_2O (2 l., 9:1) gave a small amount of wax which was not investigated further. *n*-Hexane–Et_2O (1 l., 42.5:7.5) eluted pseudocyphellarin A (0.8 g, 0.4%), *n*-hexane–Et_2O (2 l., 4:1) an oily mixture of triacylglycerols (0.73 g, 0.36%) and *n*-hexane–Et_2O (1 l., 0.7:0.3) pseudocyphellarin B. Further elution of the column with *n*-hexane–Et_2O (2 l., 1:1) gave 3-oxostictan-22α-ol, mp 213–215° (0.4 g; 0.2%) and 2α-acetoxystictan-3β,22-diol, mp 214–216° and $[\alpha]_D^{24} - 33°$ ($CHCl_3$; *c* 0.75) (1.33 g; 0.67%). Elution of the column with Et_2O–MeOH (500 ml, 9:1)

Table 1. ^1H NMR chemical shifts of the methyl groups in compounds **3**–**7**, **9** and **11**–**14**

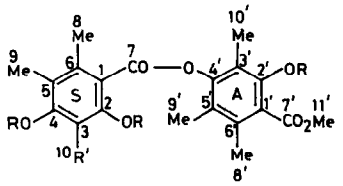
Compound	Chemical shift of the methyl group at C-3′ C-3	C-5′ C-5	C-6′ respectively C-6
Pseudocyphellarin A (**5**)	2.45	2.70	2.15
Pentaacetylpseudocyphellarin A (**6**)	2.45	2.36	2.14
Tri-*O*-methylpseudocyphellarin A (**7**)	2.40	2.22	2.19
Hypopseudocyphellarin A (**9**)	2.40	2.65	2.29
Pseudocyphellarin B (**11**)	2.35	2.57	2.11
Tetraacetylpseudocyphellarin B (**12**)	2.44	2.32	2.12 or 2.17
Nephroarctin (**13**)	2.27	2.73	2.10
Methyl 2,4-dihydroxy-3,5,6-trimethylbenzoate (**3**)	2.40	2.11	2.11
2,4-Dihydroxy-3,5,6-trimethylbenzene (**4**)	2.15	2.10	2.07
2,4-Dihydroxy-3,6-dimethylbenzene (**14**)	2.30	—	2.00



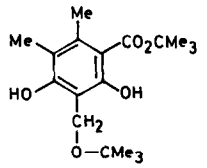
1 R = CO_2CMe_3, R' = H
2 R = R' = H
8 R = CO_2H, R' = Me



3: R = CO_2Me
4: R = H



5 R = H, R' = CHO
6 R = Ac, R' = $CH(OAc)_2$
7 R = Me, R' = CHO
9 R = H, R' = Me
11 R = H, R' = CH_2OH
12 R = Ac, R' = CH_2OAc



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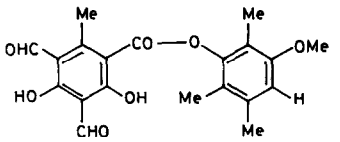

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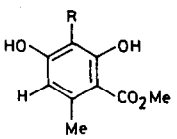

14 R = Me
15 R = H

gave stictan-2α,3β,22α-triol, mp 256–257° and $[\alpha]_D^{24}$ +6° ($CHCl_3$; *c* 0.3) (50 mg; 0.02%).

Extraction of the lichen with Me_2CO gave after recrystallization from EtOH a mixture of polyols as needles, mp 148–152° (90 mg; 0.04%).

Pseudocyphellarin A (**5**). Prisms, mp 173–175° (from Me_2CO) and the following colour reactions: KOH yellow, *p*-phenylenediamine yellow and $FeCl_3$ (in EtOH) red-brown. R_f = 0.67 (silica gel Merck PF 254 + 366, *n*-hexane–Et_2O–HCO_2H, 30:20:6, grey spot after heating with SO_3HCl–HOAc). $C_{21}H_{22}O_8$ (402.4). IR ν_{max}^{KBr} cm^{-1}: 740, 782, 810, 852, 890, 926, 942, 1010, 1030, 1070, 1092, 1116, 1190, 1290, 1312, 1428, 1640, 2980, 3400. MS *m/z* (rel. int.): 402 $[M]^+$ (6), 210.0896 $[a]^+$ (97); calc. for $C_{11}H_{14}O_4$: 210.0892, 178.0633 $[b]^+$ (100); calc. for $C_{10}H_{10}O_3$: 178.0630, 164.0474 $[c]^+$ (50); calc. for $C_9H_8O_3$: 164.0473, 150.0684 $[d]^+$ (92); calc. for $C_9H_{10}O_2$: 150.0682, 136.0522 $[e]^+$ (16); calc. for $C_8H_8O_2$: 136.0524. ^{13}C NMR (50.32 MHz, $CDCl_3$): C-1: δ 102.9 (*s*), C-2: 167.0 (*s*), C-3: 108.0 (*s*), C-4: 166.1, C-5: 118.2 (*s*), C-6: 151.5 (*s*), C-7: 169.7 (*s*), C-8: 18.8 (*q*), C-9: 10.7 (*q*), C-10: 194.0 (*d*), C-1′: 116.2 (*s*), C-2′: 159.0 (*s*), C-3′: 111.9 (*s*), C-4′: 150.1 (*s*), C-5′: 120.5, C-6′: 137.6 (*s*), C-7′: 172.1 (*s*), C-8′: 20.4 (*q*), C-9′: 13.2 (*q*), C-10′: 9.7 (*q*), C-11′: 52.3 (*q*).

Pseudocyphellarin B (**11**). Needles, mp 168–169° (dec.) and a blue-violet colour reaction with $FeCl_3$ (in EtOH). $C_{21}H_{24}O_8$ (404.4). UV λ_{max}^{MeOH} nm (log ε): 226 (4.30), 275 (4.25), 318 (3.93); $\lambda_{max}^{MeOH+NaOH}$ nm (log ε): 228 (4.30), 245 (4.20), 322 (4.41). IR ν_{max}^{KBr} cm^{-1}: 740, 776, 804, 890, 966, 990, 1002, 1070, 1092, 1110, 1170, 1240, 1260, 1318, 1440, 1578, 1604, 1640, 2960, 3250, 3550. MS, *m/z* (rel. int.): 210.0896 $[a]^+$ (83); calc. for $C_{11}H_{14}O_4$: 210.0892, 178.0632 $[b]^+$ (92); calc. for $C_{10}H_{10}O_3$: 178.0630, 150.0691 $[d]^+$ (100); calc. for $C_9H_{10}O_2$: 150.0692.

tert.-*Butanolysis of* **5**. **5** (0.18 g) in *tert.*-BuoH was heated under reflux for 48 hr. After this time TLC showed the presence of three products with R_f values 0.88 (A), 0.60 (B) and 0.52 (C), A and B being the main products. The residue after removal of solvent was dissolved in C_6H_6 and chromatographed on silica gel (7 g, with 5% H_2O); C_6H_6 (100 ml) eluted *tert.*-butyl 2,4-dihydroxy-3-formyl-5,6-dimethylbenzoate (A, **1**) as needles, mp 117–119° (from *n*-hexane), and the following colour reactions: KOH yellow to yellow-orange, *p*-phenylenediamine yellow, $FeCl_3$ (in EtOH) dirty green, on dilution with H_2O dirty blue, KOH + NaOCl orange-red. $C_{14}H_{18}O_5$ (266.3). UV λ_{max}^{MeOH} nm (log ε): 243 (4.63), 269 (4.56), S 290 (4.40); $\lambda_{max}^{MeOH+NaOH}$ nm (log ε): 220 (4.54), 292 (4.47), 410 (4.04). MS *m/z* (rel. int.): 266 $[M]^+$ (30), 210 $[f]^+$ (97), 192 $[g]^+$ (83), 164 $[c]^+$ (100), 136 $[e]^+$ (53), 108 $[h]^+$ (24). Further elution of the column with C_6H_6 (100 ml) gave methyl 2,4-dihydroxy-3,5,6-trimethylbenzoate (B, **3**) as needles, mp 92–94° (from *n*-hexane), and the following colour reactions: NaOCl deep red, $FeCl_3$ (in EtOH) blue. $C_{11}H_{14}O_4$ (210.2). UV λ_{max}^{MeOH} nm (log ε): 226 (4.71), 270 (4.66), 314 (4.24); $\lambda_{max}^{MeOH+NaOH}$ nm (log ε): 221 (4.66), 246 (4.58), 317 (4.89). MS *m/z* (rel. int.): 210 $[M]^+$ (91), 178 $[b]^+$ (100), 150 $[d]^+$ (98), 122 $[i]^+$ (63). Finally C_6H_6 (300 ml) eluted 2,4-dihydroxy-3-formyl-5,6-dimethylbenzene (C, **2**) as yellow needles, mp 137–139° (from *n*-hexane). $C_9H_{10}O_3$ (166.2). IR ν_{max}^{KBr} cm^{-1}: 702, 730, 756, 840, 892, 1000, 1100, 1204, 1242, 1290, 1340, 1380, 1416, 1444, 1510, 1598, 1626, 2920, 3200. ^1H NMR (200 MHz, $CDCl_3$): δ 2.04 (*s*, 3H, C-5-Me), 2.22 (*s*, 3H, C-6-Me), 6.14 (*s*, 1H, aromatic-H), 10.27 (*s*, 1H, –CHO). MS *m/z* (rel. int.): 166 $[M]^+$ (100), 151 $[M-Me]^+$ (72), 137 $[M-CO-H]^+$ (68).

Hydrolysis of tert.-*butyl* 2,4-*dihydroxy*-3-*formyl*-5,6-*dimethylbenzoate*. **1**, (0.12 g) was heated with KOH (0.3 g) in H_2O (2.5 ml) under H_2 under reflux for 8 hr. After usual work-up and chromatography on silica gel (6 g, with 5% H_2O), C_6H_6 (500 ml) eluted 2,4-dihydroxy-3-formyl-5,6-dimethylbenzene (**2**) as yellow needles, mp 137–139° (from *n*-hexane), identical with compound C from the *tert.*-butanolysis of pseudocyphellarin A.

The 2,4-dinitrophenylhydrazone of **2** was orange-red needles, mp 285–287° (dec., from EtOH–EtOAc). Robertson and Whalley [5] reported mp 140° for the aldehyde **2** and mp 289° for the corresponding 2,4-dinitrophenylhydrazone. IR ν_{max}^{KBr} cm^{-1}: 710, 744, 820, 840, 912, 930, 970, 1004, 1080, 1130, 1144, 1220, 1240, 1270, 1304, 1330, 1380, 1422, 1460, 1500, 1518, 1610, 2980, 3150, 3350, 3500.

Hydrolysis of methyl 2,4-*dihydroxy*-3,5,6-*trimethylbenzoate*. **3** (0.1 g) was heated with KOH (0.6 g) in H_2O (5 ml) under H_2 under reflux for 2 hr. After usual work-up and chromatography on silica gel (5 g, with 5% H_2O), C_6H_6 (100 ml) eluted 2,4-dihydroxy-3,5,6-trimethylbenzene (**4**), silk-like needles, mp 145–146° (from Et_2O–*n*-hexane). $C_9H_{12}O_2$ (152.2).

IR ν_{max}^{KBr} cm^{-1}: 840, 922, 1002, 1030, 1078, 1160, 1200, 1240, 1290, 1318, 1380, 1468, 1510, 1590, 1622, 2980, 3300, 3500. ^1H NMR (100 MHz, $CDCl_3$): δ 2.07, 2.10, 2.15 (3 × *s*, 3 × 3H, 3 × –Me), 5.87, 6.25 (2 × *s*, 2 × 1H, 2 × –OH), 7.30 (*s*, 1H, aromatic –H).

Pentaacetylpseudocyphellarin A (**6**). From **5** (0.1 g) and Ac_2O–H_2SO_4 (2 ml of a mixture of 5 ml Ac_2O and 1 drop of conc. H_2SO_4) at room temp. in 24 hr. After usual work-up and crystallization from $CHCl_3$–MeOH, prismatic plates, mp 198–200°. $C_{31}H_{32}O_{14}$ (628.6). IR ν_{max}^{KBr} cm^{-1}: 790, 870, 900, 918, 1008, 1070, 1080, 1104, 1150, 1200, 1228, 1270, 1322, 1370, 1440, 1580, 1602, 1760, 2990, 3520. ^1H NMR (100 MHz, $CDCl_3$): δ 2.02 (*s*, 9H, 3 × –Me), 2.08, 2.14 (2 × *s*, 2 × 3H, 2 × –Me), 2.23 (*s*, 9H, 3 × –Me), 2.36, 2.45 (2 × *s*, 2 × 3H, 2 × –Me), 3.84 (*s*, 3H, $-CO_2Me$)

Tri-O-methylpseudocyphellarin A (**7**). To **5** (0.13 g) and K_2CO_3 (0.5 g) in DMF (3 ml) was added Me_2SO_4 (0.25 ml) and the mixture heated at 100° for 10 min. K_2CO_3 (0.3 g) and Me_2SO_4 (0.2 ml) were then added and heating was continued for 15 min. After dilution with H_2O, the ppt. was collected by filtration, dried at room temp. and chromatographed in C_6H_6 on silica gel (5 g, with 5% H_2O); C_6H_6 (400 ml) eluted the tri-*O*-methyl ether, prisms, mp 150–152° (from $CHCl_3$–*n*-hexane). $C_{24}H_{28}O_8$ (444.5). IR ν_{max}^{KBr} cm^{-1}: 782, 830, 870, 910, 936, 958, 984, 1010, 1030, 1072, 1100, 1154, 1204, 1280, 1292, 1368, 1332, 1390, 1466, 1578, 1684, 1730, 3000. ^1H NMR (100 MHz, $CDCl_3$): δ 2.19 (*s*, 6H, 2 × –Me), 2.22 (*s*, 6H, 2 × –Me), 2.40 (*s*, 3H, –Me), 3.75, 3.84 (2 × *s*, 2 × 3H, 2 × –OMe), 3.91 (*s*, 6H, –OMe, $-CO_2Me$), 10.32 (*s*, 1H, –CHO).

2,4-Dimethoxy-3-formyl-5,6-dimethylbenzoic acid (**8**). By saponification of **7** (20 mg) with KOH (0.5 g) in MeOH (5 ml) under reflux for 2 hr. The reaction mixture was acidified with 10% H_2SO_4, extracted with Et_2O, the Et_2O extract shaken with $NaHCO_3$ soln (5%), the $NaHCO_3$ extract acidified and again extracted with Et_2O. The Et_2O was removed and the residue twice recrystallized from MeOH–H_2O: prisms, mp 112–115°. $C_{12}H_{14}O_5$ (238.2). IR ν_{max}^{KBr} cm^{-1}: 760, 902, 952, 984, 1010, 1046, 1090, 1110, 1190, 1290, 1380, 1410, 1464, 1580, 1682, 1722, 3000, 3200. MS *m/z* (rel. int.): 238 $[M]^+$ (100), 220 $[M-H_2O]^+$ (67), 205 $[M-H_2O-Me]^+$ (53), 177 $[M-H_2O-Me-CO]^+$ (40).

Hypopseudocyphellarin A (**9**). By hydrogenation of **5** (0.1 g) in EtOAc (30 ml) with 10% Pd/C (0.1 g) under normal conditions for 6 hr and chromatography of the resulting product on silica gel (6 g, with 5% H_2O). After elution with C_6H_6 (200 ml), Et_2O (200 ml) eluted hypopseudocyphellarin A, rectangular prisms, mp 172–173° (dec., from $CHCl_3$–MeOH). $C_{21}H_{24}O_7$ (388.4). IR ν_{max}^{KBr} cm^{-1}: 746, 780, 810, 900, 970, 990, 1010, 1030, 1070, 1100, 1114, 1170, 1240, 1262, 1310, 1398, 1444, 1580, 1610, 1640, 3020, 3250, 3550. ^1H NMR (100 MHz, DMSO-d_6): δ 2.29 (*s*, 6H, 2 × –Me), 2.34, 2.40, 2.65, 3.59 (4 × *s*, 4 × 3H, 4 × –Me), 4.10 (*s*, 3H, $-CO_2Me$), 9.40, 9.97, 10.59 (3 × *s*, 3 × H, 3 × –OH).

tert.-*Butanolysis of pseudocyphellarin B*. **11** (50 mg) in *tert.* BuOH (50 ml) was heated under reflux for 24 hr. The residue after removal of the solvent was separated by prep. TLC. (silica gel, Merck PF 254 + 366, 10 × 10 × 0.1 cm, *n*-hexane–Et_2O–HCO_2H, 30:20:3) and showed two main bands of R_f values 0.56 (A) and 0.80 (B). Elution of band A gave 2,6-dihydroxy-3,4-dimethyl-5-*tert.*-butoxycarbonyl-1-benzyl-*tert.*-butyl ether (**10**), needles, mp 69–70° (from MeOH–H_2O). $C_{18}H_{28}O_5$ (324.4). IR ν_{max}^{KBr} cm^{-1}: 762, 784, 844, 878, 894, 1006, 1050, 1084, 1116, 1150, 1220, 1260, 1286, 1336, 1360, 1394, 1464, 1570, 1624, 3000, 3220, 3500. ^1H NMR (100 MHz, $CDCl_3$): δ 1.28, 1.56 (2 × *s*, 2 × 9H, 2 × $-CMe_3$), 2.03, 2.36 (2 × *s*, 2 × 3H, 2 × –Me), 4.78 (*s*, 2H, $-CH_2-O-$), 9.65, 11.61 (2 × *s*, 2 × H, 2 × –OH). MS *m/z* (rel. int.): 324 $[M]^+$ (75), 268 $[M-CH_2=CMe_2]^+$ (77), 250 $[M-CH_2=CMe_2-H_2O]^+$ (62), 232 $[M-CH_2=CMe_2-2H_2O]^+$ (45), 194 $[M-2CH_2=CMe_2-H_2O]^+$ (100), 176 $[M-2CH_2=CMe_2-2H_2O]^+$ (98), 166 $[M-2CH_2=CMe_2-H_2O-CO]^+$ (75). Elution of band B gave needles, mp 92–94° (from *n*-hexane), identical with 2,4-dihydroxy-3,5,6-trimethylbenzoate (**3**) in all respects.

Tetraacetylpseudocyphellarin B (**12**). From **11** (35 mg) and Ac_2O–H_2SO_4 (1 ml of a mixture of 5 ml Ac_2O and 1 drop of conc. H_2SO_4) at room temp. in 24 hr. After usual work-up and crystallization from MeOH, small prisms, mp 145–146°. $C_{29}H_{32}O_{12}$ (572.5). IR ν_{max}^{KBr} cm^{-1}: 796, 880, 920, 1030, 1074, 1150, 1180, 1206, 1244, 1268, 1324, 1372, 1440, 1574, 1608, 1730, 1762, 2980.

GC/MS analysis of triacylglycerols. Part of the mixture of triacylglycerols from *P. endochrysea* (0.1 g) was hydrolysed with KOH–MeOH and the resulting mixture of fatty acids converted into the corresponding methyl esters with CH_2N_2. GC/MS (10% EGSS-X on Gaschrom P, 125–150 μm, glass column, 2 mm i.d., 180 cm, T = 160°) showed the presence of methyl palmitate (24%, *m/z* 270, $C_{17}H_{34}O_2$), methyl stearate (3%, *m/z* 298, $C_{19}H_{38}O_2$), methyl oleate (31%, *m/z* 296, $C_{19}H_{36}O_2$), methyl linoleate (35%, *m/z* 294, $C_{19}H_{34}O_2$) and methyl linolenate (5%, *m/z* 292, $C_{19}H_{32}O_2$).

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