Scensidin, a New Depsidone from the Lichen *Buellia canescens* (Dicks.) De Not

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The biogenetically favoured constitution (4) for scensidin isolated from *Buellia canescens* has been established by total synthesis. Intramolecular oxidative coupling of the tetrahydroxybenzophenone (22) yields the grisadienedione (23) which, by thermal isomerisation (23) ⟶ (25) followed by methylation, yields scensidin (4). Alternatively, methylation of the grisadienedione (23) followed by thermal isomerisation also yields scensidin.

The transformation of the grisadienedione (26) into the dibenzofuran (28) occurs both thermally and photochemically.

The first phytochemical examination of the lichen *Buellia canescens* was carried out by Zopf,[1] who isolated diploicin (1) and atranorin (11). Nolan and his co-workers [2] re-examined the same species grown in Ireland and confirmed the presence of these two compounds. In addition to these compounds mannitol, the depside chloroatranorin (12), and a trichloro-analogue ($C_{16}H_{11}Cl_3O_5$, structure unknown) of diploicin (1) were also reported.

Devlin [3] and Smith [3] also examined the same lichen collected in south Devonshire. In addition to the compounds previously characterised, three further depsidones, dechlorodiploicin (2), dechlorodiploicin *O*-methyl ether (3), and scensidin were isolated.[3] In a recent investigation of the same species from Australia, the three depsidones (1)—(3) and two new phthalides, buellolide and canesolide, have been reported.[4]

Of the four depsidones isolated from *Buellia canescens* the structure of diploicin as (1) has been unambiguously established by two different syntheses.[5,6] The structures of the depsidones (2) and (3) have been determined by degradative studies [3,4] as well as by total synthesis.[7,8] We now report a total synthesis of scensidin which establishes its structure as (4).

Results and Discussion

Scensidin.—The initial indication that scensidin possessed a depsidone skeleton was revealed by its i.r. spectrum [$\nu_{max.}$ ($CHCl_3$) 1 740 cm^{-1}, lactone C=O]. An accurate mass spectrum established the molecular formula as $C_{17}H_{14}Cl_2O_5$. The ^1H n.m.r. spectrum showed singlets at δ ($CDCl_3$) 6.67 and 6.63 (each 1 H), 3.91 and 3.81 (each 3 H), and 2.49 (6 H). As scensidin occurs together with the depsidones (1), (2), and (3) in *B. canescens*, it was biogenetically reasonable to believe that scensidin would be a depsidone of this type rather than of the type to which variolaric acid belongs.[9,10] Six biogenetically reasonable structures, (4)—(9), were considered as plausible for scensidin.

The mass spectrum of scensidin showed fragment ions as *m/z* 198 (13) and *m/z* 199 (14) which indicated that the compound possesses one chloro-substituent on each of the aromatic rings, *i.e.* apparently eliminating structures (5) and (6). This preliminary conclusion was further supported by a comparison of the ^1H n.m.r. spectral data of scensidin with those of authentic samples of the depsidones (5) [11] and (6).[12] Compounds (5) and (6) both showed a signal due to one pair of *meta*-coupled aromatic protons. In contrast, scensidin showed two singlets (δ 6.67 and 6.63) each corresponding to one aromatic proton. These results conclusively excluded structures (5) and (6) for scensidin. All known naturally occurring dichloro-depsidones with one chlorine atom associated with each aromatic ring have these atoms located at positions 2 and 7.[9,10,13] Structure (4) for scensidin was therefore favoured in biogenetic grounds and this compound was selected as a target for total synthesis.

Synthesis of Scensidin.—Condensation of 2,4-di-*O*-benzyl-5-chloro-orsellinic acid † (18) and 3,5-dibenzyloxy-2-chlorotoluene (20) in boiling trifluoroacetic anhydride (TFAA) for two days gave the benzophenone (21) (56% yield), hydrogenolysis of which gave the symmetrical tetrahydroxybenzophenone (22). Treatment of this compound with potassium hexacyanoferrate(III) in aqueous potassium carbonate at room temperature for 5 min gave the crystalline grisa-3′,5′-diene-2′,3-dione (23) (54% yield). After collection of the crystalline oxidation product (23), the mother-liquors, on treatment with diazomethane, gave a mixture from which the conjugated grisa-3′,5′-diene-2′,3′-dione (26) and the cross-conjugated grisa-2′,5′-diene-3,4′-dione (27) were isolated.

It has been observed that grisa-3′,5′-diene-2′,3-diones, when heated to just above their m.p.s, are smoothly isomerised into the corresponding depsidones.[4,7] When the grisa-3′,5′-diene-2′,3-dione (23) was heated at 175 °C it gave the depsidone (25) (23% yield). Methylation of the depsidone (25) with diazomethane gave scensidin (4), identical with the natural product.

The grisa-3′,5′-diene-2′,3-dione (23) could, in principle, exist in equilibrium with its cross-conjugated tautomer (24). However, the crystalline compound (23) and diazomethane gave only one dimethyl ether (26) (88% yield). When the grisa-3′,5′-diene-2′,3-dione (26) was heated at 220—230 °C, it gave not only the depsidone scensidin (4) (32% yield), but also the dibenzufuran (28) (24% yield). Dibenzofurans have been shown to be formed by the photolysis [7,14] of grisa-3′,5′-diene-2′,3-diones, but no case has yet been reported where this transformation has been achieved thermally. The dibenzofuran (28) was the sole product (41% yield) when compound (26) was irradiated in benzene solution at room temperature using a 450-W medium-pressure mercury lamp.

The formation of the dibenzofuran (28) and the depsidone (4) by the action of heat on compound (26) may well involve either concerted sigmatropic rearrangements or reactions involving biradical intermediates.[7,8,14]

The grisa-3′,5′-diene-2′,3-dione (23), when kept in aqueous methanol for three days, yielded the 4′-methoxygrisa-3′,5′-diene-2′,3-dione (30) and some starting material. This reaction presumably involved the hemiacetal (29) as an intermediate. The total product [a mixture of compounds (23) and (30)] was

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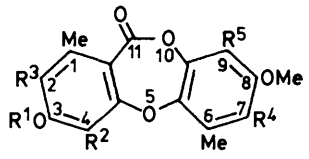
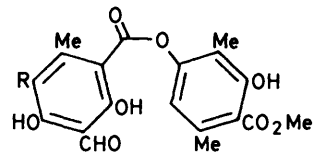
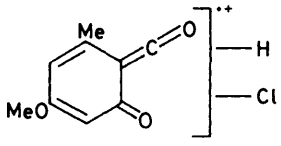
† Orsellinic acid is 2,4-dihydroxy-6-methylbenzoic acid.



(1) $R^1 = H, R^2 = R^3 = R^4 = R^5 = Cl$ (Diploicin)
(2) $R^1 = R^2 = H, R^3 = R^4 = R^5 = Cl$ (Dechlorodiploicin)
(3) $R^1 = Me, R^2 = H, R^3 = R^4 = R^5 = Cl$ (Dechlorodiploicin *O*-methyl ether)
(4) $R^1 = Me, R^2 = R^5 = H, R^3 = R^4 = Cl$ (Scensidin)
(5) $R^1 = Me, R^2 = R^3 = Cl, R^4 = R^5 = H$
(6) $R^1 = Me, R^2 = R^3 = H, R^4 = R^5 = Cl$
(7) $R^1 = Me, R^2 = R^5 = Cl, R^3 = R^4 = H$
(8) $R^1 = Me, R^2 = R^4 = Cl, R^3 = R^5 = H$
(9) $R^1 = Me, R^2 = R^4 = H, R^3 = R^5 = Cl$
(10) $R^1 = H, R^2 = R^5 = H, R^3 = R^4 = Cl$



(11) R = H (Atranorin)
(12) R = Cl (Chloroatranorin)



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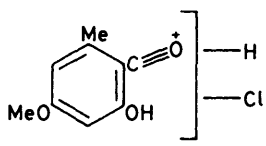


(14)

heated at 150—158 °C to give the depsidone (25) and (10) without any detectable formation of the corresponding dibenzofurans.

Experimental

M.p.s were determined using a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded using a Perkin-Elmer 157G spectrophotometer. U.v. spectra were measured using a Cary-14 spectrometer. ^1H N.m.r. spectra were obtained using a Varian HA.100 spectrometer and tetramethylsilane as internal standard. For column chromatography and t.l.c., Merck silica gel (Kieselgel G) was used. Light petroleum refers to the fraction of boiling in the range 60—80 °C.

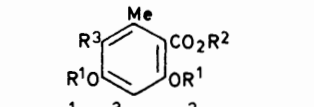
Extraction of the Total Lichen Buellia canescens (*Dicks.*) *De Not (with J. P. Devlin* [3] *and C. Smith* [3]).—The lichen material which was originally examined was donated to Professor W. D. Ollis from the collection of the late Professor T. J. Nolan, University College, Dublin.[2] Similar results were obtained with lichen material subsequently collected from south Devonshire.

The powdered lichen material (400 g) was extracted with (i) cold diethyl ether (2 l; 2 h), (ii) cold diethyl ether (2 l; 2 d), (iii) boiling diethyl ether (2 l; 2 d), and (iv) boiling dichloromethane (2 l; 2 d) to give, after work-up of the respective fractions, four residues (i) (18.90 g), (ii) (3.1 g), (iii) (1.10 g), and (iv) (3.35 g). Fractionation of these residues by a combination of trituration, column chromatography, preparative t.l.c., and crystallisation eventually yielded diploicin (1) (4.88 g), m.p. 231—232 °C (lit.,[2] 232 °C; lit.,[4] 231—232 °C); dechlorodiploicin (2) (62 mg), m.p. 263—265 °C (lit.,[2] 263—265 °C; lit.,[4] 272.5—274 °C); dechlorodiploicin *O*-methyl ether (3) (28 mg), m.p. 226—228 °C (lit.,[4] 230—231.5 °C); atranorin (11) (120 mg), m.p. 185—197 °C (lit.,[9] 196—197 °C); and chloroatranorin (12) (87 mg), m.p. 208—210 °C (lit.,[9] 208—208.5 °C). These compounds were fully characterised by their mass-, n.m.r.-, u.v.-, and i.r.-spectra, and a comparison with published spectral data [4] established their identity. The identities of dechlorodiploicin (2) and dechlorodiploicin *O*-methyl ether (3) were established by synthesis.[7,8] This extraction procedure also yielded a new natural depsidone which we have named scensidin (4) (31 mg) as needles, m.p. 199—201 °C (from methanol) (Found: $M^{\cdot+}$, 368.8990 $C_{17}H_{14}Cl_2O_5$ requires *M*, 369.202); $\nu_{max.}$ ($CHCl_3$) 1 740 cm^{-1}; δ ($CDCl_3$) 6.67 (1 H, s, ArH), 6.63 (1 H, s, ArH), 3.91 (3 H, s, OMe), 3.81 (3 H, s, OMe), and 2.49 (6 H, s, 2 × Me).

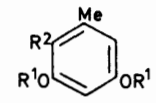
Ethyl 5-Chloro-orsellinate (16).—A solution of ethyl orsellinate (15) (10 g, 0.051 mol) in dry diethyl ether (150 ml) was treated dropwise at room temperature with a solution of sulphuryl chloride (4.0 ml, 0.050 mol) in dry diethyl ether (4.0 ml). After the addition, the solution was stirred at room temperature for 1 h and was then gently boiled for 45 min. The cooled ethereal solution was then treated dropwise with water and the mixture was shaken. The organic phase, was separated and was washed with water, dried ($MgSO_4$), and evaporated to dryness. The solid residue (11.4 g) was fractionated on a silica-gel column with benzene as eluant. Crystallisation of the eluate from aqueous ethanol gave ethyl 5-chloro-orsellinate (16) (7.4 g, 63%), m.p. 135—136 °C (lit.,[15] 128 °C); $\nu_{max.}$ ($CHCl_3$) 3 500 and 1 665 cm^{-1}; δ ($CDCl_3$) 6.44 (1 H, s, ArH), 4.41 (2 H, q, *J* 7 Hz, CH_2Me), 2.58 (3 H, s, Ar*Me*), and 1.38 (3 H, t, *J* 7 Hz, CH_2Me).

Ethyl 2,4-*Di*-O-*benzyl*-5-*chloro-orsellinate* (17).—To a solution of compound (16) (3 g, 0.013 mol) in acetone (120 ml) were added, in turn, fused potassium carbonate (3.5 g) and benzyl bromide (2.5 ml, 0.021 mol). The mixture was stirred and heated under reflux for 18 h and was then filtered. After evaporation of the acetone from the filtrate, the excess of benzyl bromide was removed by column chromatography using light petroleum as eluant. The column was then eluted with acetone to elute the desired product. After evaporation of the acetone eluates, the product was crystallised from ethanol to give *ethyl* 2,4-*di*-O-*benzyl*-5-*chloro-orsellinate* (17) as crystals (4.85 g, 91%), m.p. 79—80 °C (Found: C, 70.2; H, 5.9; Cl, 8.7; $M^{\cdot+}$, 410. $C_{24}H_{23}ClO_4$ requires C, 70.2; H, 5.6; Cl, 8.7%; *M*, 410); $\nu_{max.}$ ($CHCl_3$) 1 723 cm^{-1}; δ ($CDCl_3$) 7.23 and 7.29 (total 10 H, 2 × s, 2 × Ph), 6.40 (1 H, s, ArH), 5.06 and 4.97 (total 4 H, 2 × s, 2 × ArCH_2), 4.31 (2 H, q, *J* 7 Hz, CH_2Me), 2.31 (3 H, s, Ar*Me*), and 1.27 (3 H, t, *J* 7 Hz, CH_2Me).

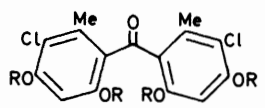
2,4-*Di*-O-*benzyl*-5-*chloro-orsellinic Acid* (18).—To a solution of the ester (17) (5.35 g, 0.013 mol) in ethanol (230 ml) was



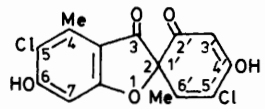
(15) $R^1 = R^3 = H$, $R^2 = Et$
(16) $R^1 = H$, $R^2 = Et$, $R^3 = Cl$
(17) $R^1 = CH_2Ph$, $R^2 = Et$, $R^3 = Cl$
(18) $R^1 = CH_2Ph$, $R^2 = H$, $R^3 = Cl$



(19) $R^1 = H$, $R^2 = Cl$
(20) $R^1 = CH_2Ph$, $R^2 = Cl$



(21) $R = CH_2Ph$
(22) $R = H$



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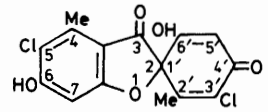

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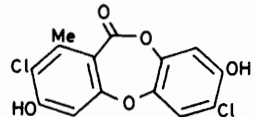

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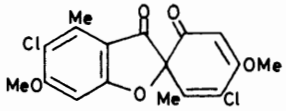

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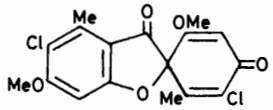

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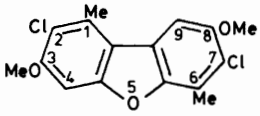

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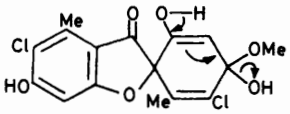

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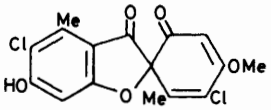

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added 10M-aqueous sodium hydroxide (100 ml). The mixture was then heated under reflux for 18 h. Ethanol was evaporated off from the cooled solution and the residue was diluted with water and acidified with dilute hydrochloric acid. The solid product was filtered off, washed with water, and crystallised from aqueous methanol to give 2,4-di-*O*-benzyl-5-chloro-orsellinic acid (18) as crystals (4.3 g, 86%), m.p. 160—161 °C (lit.,[16] 163—164 °C) (Found: C, 69.3; H, 4.9; Cl, 9.1; $M^{\cdot+}$, 382. Calc. for $C_{22}H_{19}ClO_4$: C, 69.0; H, 5.0; Cl, 9.3%; *M*, 382); $\nu_{max.}$ (KBr) 1 690 cm^{-1}; δ [$(CD_3)_2CO$] 7.38 (10 H, m, 2 × Ph), 6.86 (1 H, s, ArH), 5.20 and 5.13 (total 4 H, 2 × s, 2 × ArCH_2), and 2.33 (3 H, s, Me).

4-Chloro-oricinol * (19).—The ester (16) (3.4 g, 0.148 mol) was boiled under reflux with 5% aqueous potassium hydroxide (250 ml) for 1 h. The cooled solution was acidified and shaken with diethyl ether (2 × 100 ml). The combined extracts were washed in turn with aqueous sodium hydrogen carbonate and water and were dried ($MgSO_4$) and evaporated to dryness. The residue was crystallised from diethyl ether–η-hexane to give 4-chloro-orcinol (19) as crystals (1.9 g, 81%), m.p. 141—142 °C (lit.,[17] 138—140 °C); $\nu_{max.}$ ($CHCl_3$) 3 520 and 3 280 cm^{-1}; δ [$(CD_3)_2CO$] 8.23br (2 H, s, 2 × OH), 6.37 (H_A) and 6.31 (H_B) (together AB system, J_{AB} 3 Hz, 2 × *meta*-ArH), and 2.23 (3 H, s, Me).

4,4',6,6'-Tetrabenzyloxy-3,3'-dichloro-2,2'-dimethylbenzophenone (21).—A stirred suspension of the acid (18) (1.15 g, 0.003 mol) and 3,5-dibenzyloxy-2-chlorotoluene [8] (20) (1.2 g, 0.004 mol) in TFAA (70 ml) was heated under reflux for 2 d. From the cooled suspension, a gummy material was separated and was washed with water and crystallised from methanol to give the *title compound* (21) as crystals (1.29 g, 56%), m.p. 169—170 °C (Found: C, 73.3; H, 5.3; Cl, 10.4%; $M^{\cdot+}$, 702. $C_{43}H_{36}Cl_2O_5$ requires C, 73.4; H, 5.1; Cl, 10.1%; *M*, 702); $\nu_{max.}$ ($CHCl_3$) 1 660 cm^{-1}; δ ($CDCl_3$) 7.37 (10 H, s, 2 × Ph), 7.10 (10 H, m, 2 × Ph), 6.32 (2 H, s, 2 × ArH), 5.08 and 4.60 (total 8 H, 2 × s, 4 × ArCH_2), and 2.10 (6 H, s, 2 × Me).

3,3'-Dichloro-4,4',6,6'-tetrahydroxy-2,2'-dimethylbenzophenone (22).—A stirred solution of the benzophenone (21) (0.85 g) in ethyl acetate (80 ml) was hydrogenolysed at room temperature and atmospheric pressure for 18 h with palladium–charcoal (0.29 g, 10%). The solution was filtered, the filtrate was evaporated, and the residue was crystallised from diethyl ether–n-hexane to afford the *title compound* (22) as yellow crystals (0.36 g, 88%), m.p. 200—201 °C (Found: $M^{\cdot+}$, 342.0069. $C_{15}H_{12}Cl_2O_4$ requires *M*, 342.0076); $\nu_{max.}$ (KBr) 1 610 cm^{-1}; δ [$(CD_3)_2CO$] 6.57 (2 H, s, 2 × ArH) and 2.18 (6 H, s, 2 × Me).

5,5'-Dichloro-4',6-dihydroxy-4,6'-dimethylspiro[benzofuran-2(3H),1'-cyclohexa-3',5'-diene]-2',3-dione (23).—To a stirred solution of the tetrahydroxybenzophenone (22) (0.17g, 0.496 mmol) and potassium carbonate (1.7 g) in water (20 ml) was added in one go a solution of potassium hexacyanoferrate-(III) (0.28 g, 0.851 mmol) in water (20 ml). After being kept for 5 min at room temperature, the solution was cooled and acidified with dilute hydrochloric acid. The semi-solid precipitate was collected by filtration, washed with water, and dried. Crystallisation from diethyl ether and then from a mixture of ethyl acetate–diethyl ether gave crystals of *5,5'-dichloro-4',6-dihydroxy-4,6'-dimethylspiro[benzofuran-2(3H),1'-cyclohexa-3',5'-diene]-2',3-dione* (23) (70 mg, 54%), m.p. 193—194 °C (Found: $M^{\cdot+}$, 339.9905. $C_{15}H_{10}Cl_2O_5$ requires *M*, 339.9905); $\lambda_{max.}$ (EtOH) 233 (ε 24 600), 280 (20 000), and 322 nm (11 000); $\nu_{max.}$ (KBr) 3 400, 1 710, and 1 687 cm^{-1}; δ [$(CD_3)_2CO$] 6.77 (1 H, s, ArH), 5.72 (1 H, s, vinylic H), 2.56 (3 H, s, Ar*Me*), and 1.85 (3 H, s, 6'-Me).

3,5-Dichloro-6,6'-dimethoxy-2',4-dimethylspiro[benzofuran-2(3H),1-cyclohexa-2',5'-diene]-3,4'-dione (27) *and* *5,5'-Dichloro-4',6-dimethoxy-4,6'-dimethylspiro[benzofuran-2(3H),1'-cyclohexa-3',5'-diene]-2',3-dione* (26).—The mother-liquor from the crystallisation of compound (23) (see above) was evaporated to dryness and the residue was dissolved in acetone. Treatment of this solution with an excess of an ethereal solution of diazomethane at room temperature for 5 min and work-up in the usual way gave an oil which was fractionated by preparative t.l.c. on silica gel with chloroform as developer. The product with the lower R_F value was crystallised from ethanol to give *3',5-dichloro-6,6'-dimethoxy-2',4-dimethylspiro[benzofuran-2(3H),1'-cyclohexa-2',5'-diene]-3,4'-dione* (27) (24 mg, 12%), m.p. 232—233 °C (Found: C, 55.1; H, 4.0; Cl, 19.3%; $M^{\cdot+}$, 368. $C_{17}H_{14}Cl_2O_5$ requires C, 55.3; H, 3.8; Cl, 19.2%; *M*, 368); $\lambda_{max.}$ ($CHCl_3$) 278 (ε 17 700) and 334 nm (11 700); $\nu_{max.}$ ($CHCl_3$) 1 750, 1 660, and 1 627 cm^{-1}; δ ($CDCl_3$) 6.68 (1 H, s, ArH), 5.49 (1 H, s, vinylic H),

* 4-Chloro-5-methylresorcinol.

4.00 and 3.85 (total 6 H, 2 × s, 2 × OMe), 2.55 (3 H, s, Ar*Me*), and 1.97 (3 H, s, 2'-Me).

The product with the higher R_F value was crystallised from acetone to give 5,5'-*dichloro*-4',6-*dimethoxy*-4,6'-*dimethylspiro*[*benzofuran*-2(3H),1'-*cyclohexa*-3',5'-*diene*]-2',3-*dione* (26) as crystals (8 mg, 4%), m.p. 268—269 °C, with partial melting and change of crystal shape between 225—240 °C (Found: C, 55.1; H, 3.9; Cl, 19.3%; $M^{\cdot+}$, 368. $C_{17}H_{14}Cl_2O_2$ requires C, 55.3; H, 3.8; Cl, 19.2%; *M*, 368); $\lambda_{max.}$ ($CHCl_3$) 278 (ε 31 300) and 332 nm (69 500); $\nu_{max.}$ ($CHCl_3$) 1 720 and 1 655 cm^{-1}; δ ($CDCl_3$) 6.61 (1 H, s, ArH), 5.77 (1 H, s, vinylic H), 4.01 (3 H, s, ArO*Me*), 3.64 (3 H, s, 4'-OMe), 2.61 (3 H, s, Ar*Me*), and 1.85 (3 H, s, 6'-Me).

Methylation of the grisa-3',5'-diene-2',3-dione (23) with diazomethane in a similar way gave the grisa-3',5'-diene-2',3-dione (26) (yield 88%).

2,7-*Dichloro*-3,8-*dihydroxy*-1,6-*dimethyl*-11H-*dibenzo*[b,e][1,4]*dioxepin*-11-*one* (25).—The grisadienedione (23) (0.1 g) was heated in a preheated aluminium block at 175 °C for 0.5 h. The crude product was fractionated on silica-gel plates with chloroform–methanol (9 : 1) as eluant. The faster moving band was removed and the product was crystallised from diethyl ether–light petroleum to give 2,7-*dichloro*-3,8-*dihydroxy*-1,6-*dimethyl*-11H-*dibenzo*[b,e][1,4]*dioxepin*-11-*one* (25) as crystals which were further purified by sublimation at 220 °C and 0.02 mmHg (23 mg, 23%), m.p. 239—242 °C, (Found: $M^{\cdot+}$, 339.9902. $C_{15}H_{10}Cl_2O_5$ requires *M*, 339.9905); $\nu_{max.}$ (KBr) 1 712 cm^{-1}; δ [$(CD_3)_2CO$] 9.41br (1 H, s, OH), 6.89 and 6.77 (total 2 H, 2 × s, 2 × ArH), 2.98br (1 H, s, OH), and 2.48 (6 H, s, 2 × Me).

Scensidin (4).—A solution of the depsidone (25) (20 mg) in acetone was treated with an excess of an ethereal solution of diazomethane. After being kept 20 min at room temperature the reaction mixture was worked up in the usual way and the product was crystallised from chloroform–light petroleum to give scensidin (4) as crystals (20 mg, 92%), m.p. 199—201 °C, identical with the natural product isolated from the lichen *Buellia canescens*.

Thermolysis of the Grisadienedione (26). *Isolation of Scensidin* (4) *and* 2,7-*Dichloro*-3,8-*dimethoxy*-1,6-*dimethyldibenzofuran* (28).—The grisa-3',5'-diene-2',3-dione (26) (0.1 g) was heated at 220—230 °C for 2 h in a preheated aluminium block. The dark liquid product was distilled at 0.1 mmHg and the semi-solid product was purified (t.l.c.) on silica-gel plates with benzene–light petroleum (7 : 3) as developer. The slower moving band was removed and the product was crystallised from chloroform–light petroleum to afford scensidin (4) (32 mg, 32%), m.p. 199—201 °C.

The material in the faster moving band, after extraction and crystallisation from ethyl acetate–n-hexane, gave 2,7-*dichloro*-3,8-*dimethoxy*-1,6-*dimethyldibenzofuran* (28) (21 mg, 24%), m.p. 203—204 °C (Found: $M^{\cdot+}$, 325.0318. $C_{16}H_{14}Cl_2O_5$ requires *M*, 325.0320); $\nu_{max.}$ ($CHCl_3$) 1 628 and 1 590 cm^{-1}; δ ($CDCl_3$) 7.25 and 6.96 (total 2 H, 2 × s, 2 × ArH), 3.97 (6 H, s, 2 × OMe), and 2.77 and 2.57 (total 6 H, 2 × s, 2 × Me).

Photolysis of the Grisa-3',5'-*diene*-2',3-*dione* (26).—A solution of compound (26) (50 mg) in dry benzene (10 ml) was irradiated in a quartz tube at room temperature using a Hanovia medium-pressure mercury lamp (450 W) for 20 h. T.l.c. examination of the product on silica gel with benzene–light petroleum (7 : 3) as developer showed the presence of the starting grisadienedione (26), the dibenzofuran (28), and some polymeric material. The mixture was fractionated as described above and yielded the dibenzofuran (28) (18 mg, 41%), m.p. 203—204 °C.

2,7-*Dichloro*-3-*hydroxy*-8-*methoxy*-1,6-*dimethyl*-11H-*dibenzo*[b,e][1,4]*dioxepin*-11-*one* (10).—A solution of the grisadienedione (23) (0.12 g) in methanol (4 ml) containing water (8 drops) was kept at 5 °C for 3 d, after which the crystalline solid which had formed was collected by filtration. Examination of the ^1H n.m.r. spectrum of the dried product showed it to be a mixture of the starting grisadienedione (23) and 5,5'-*dichloro*-6-*hydroxy*-4'-*methoxy*-4,6'-*dimethylspiro*[*benzofuran*-2(3H),1'-*cyclohexa*-3',5'-*diene*]-2',3-*dione* (30); δ [compound (30)] [$(CD_3)_2CO$] 6.83 (1 H, s, ArH), 5.77 (1 H, s, vinylic H), 3.33 (3 H, s, 4'-OMe), 2.58 (3 H, s, ArMe), and 1.87 (3 H, s. 6'-Me).

This mixture (50 mg) of the grisadienediones (23) and (30) was heated at 150—158 °C for 30 min and the crude product was fractionated by thick-layer chromatography with chloroform–ethyl acetate (95 : 5) as developer. The faster moving band gave 2,7-dichloro-3,8-dihydroxy-1,6-dimethyl-11*H*-dibenzo[*b*,*e*][1,4]dioxepin-11-one (25) (18 mg). The slower moving band gave 2,7-*dichloro*-3-*hydroxy*-8-*methoxy*-1,6-*dimethyl*-11H-*dibenzo*[b,e][1,4]*dioxepin*-11-*one* (10) as an oil (8 mg) which failed to crystallise (Found: $M^{\cdot+}$, 354.0060. $C_{16}H_{12}Cl_2O_5$ requires *M*, 354.0062); $\nu_{max.}$ ($CHCl_3$) 1 710 cm^{-1}; δ [$(CD_3)_2CO$] 6.56 and 6.10 (total 2 H, 2 × s, 2 × ArH), 3.90. (3 H, s, OMe), and 2.32 and 2.14 (total 6 H, 2 × s, 2 × Me).

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