Pigments of Fungi. Part 12.[1,2] Structure and Absolute Stereochemistry of Antibiotic Tetrahydroanthraquinones from the Fungus *Dermocybe splendida* Horak. X-Ray Structure Determination of Austrocortirubin Phenylboronate and Austrocortilutein Acetonide

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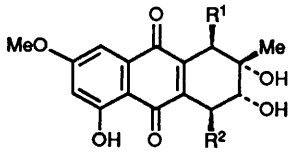
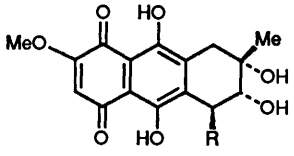
(1*S*,3*S*)-(+)-Austrocortirubin (**6**), (1*S*,3*S*)-(+)-austrocortilutein (**8**) and (1*S*,3*R*)-(+)-austrocortilutein (**10**) have been isolated from fresh fruit bodies of the fungus *Dermocybe splendida* and their structures established by chemical, spectroscopic, and X-ray crystallographic methods. Absolute stereochemistry has been established by chemical correlation with (2*R*)-methyl 2-(2'-methyl-5'-oxotetrahydrofuryl)acetate (**27**) and confirmed by single crystal X-ray analysis of the acetonide derivative (**23**) of (1*S*,3*S*)-austrocortilutein. The tetrahydroanthraquinones (**6**), (**8**) and (**10**) are active at low concentration against a range of bacteria and fungi.

The naturally occurring tetrahydroanthraquinones altersolanol-A (**1**), altersolanol-B (**2**), dactylariol (**3**), bostrycin (**4**), and 4-deoxybostrycin (**5**) constitute a small family of potent antibiotics restricted in their distribution to a group of predaceous, ascomycetious conidial fungi. The first members of the family, the altersolanols -A (**1**) and -B (**2**), were isolated from cultures of *Alternaria solani*, the causative agent of early blight disease of potato[3] and a pathogen of other solanaceous plants. Both of the altersolanols occur together with dactylariol (**3**) in cultures of *Dactylaria lutea*, extracts of which are active against protozoa and nematodes.[4] The antibacterial agent bostrycin (**4**) was first characterised from the culture broth of *Bostrychonema alpestre*,[5] and occurs together with its 4-deoxy analogue (**5**) in *Alternaria eichhorniae*, the organism responsible for leaf blight on the water hyacinth *Eichhorniae crassipea*.[6]



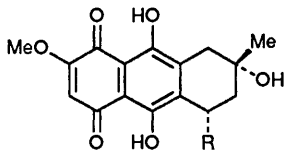
(1) $R^1 = R^2 = OH$
(2) $R^1 = R^2 = H$
(3) $R^1 = OH$, $R^2 = H$



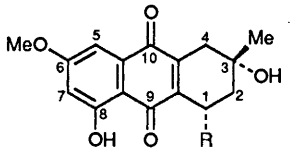
(4) R = OH
(5) R = H

We report here the isolation from an Australasian toadstool of three new tetrahydroanthraquinones to which structures (**6**), (**8**), and (**10**) are assigned on chemical and spectroscopic grounds, and confirmed by single crystal X-ray analyses. These pigments are the first tetrahydroanthraquinones to be found in Basidiomycetes.

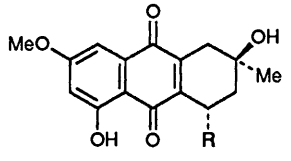
The fungus *Dermocybe splendida* produces conspicuous fruit bodies consisting of a deep red cap with an underlying network of brilliant orange gills. The cap is joined to a long stipe which is red near the top and bears deep red ring zones. The stipe becomes chrome yellow closer to the base and terminates in a mat of rich yellow mycelium. Photographs of the fruit bodies have been published.[7] Prior to the commencement of our studies the type collection of *D. splendida* from New Zealand[8] had been examined using analytical TLC by Keller[9] who concluded that the pigments produced by this fungus bore no resemblance to any of the numerous anthraquinones detected previously in toadstools belonging to *Dermocybe*† or *Cortinarius*.[10]



(6)R = OH
(7)R = H



(8)R = OH
(9)R = H



(10)R = OH
(11)R = H

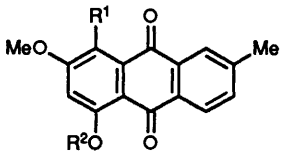
For our work fruit bodies of *D. splendida* were collected from mixed *Eucalyptus* forest near Marysville, Victoria beginning in July 1984. The fresh fungus was finely chopped and immersed in alcohol overnight. Evaporation of the deep red extracts gave an aqueous suspension which was washed with petrol and then extracted with ethyl acetate. Although some colour remained in the aqueous phase, the bulk of the pigmented material passed into the organic layer. Preliminary TLC on silica gel separated a minor, mobile zone consisting predominantly of the anthraquinones (**12**) and (**13**)[12] from a major, polar zone containing among other pigments,[13] the tetrahydroanthraquinones (**6**), (**8**), and (**10**). The individual constituents of this mixture were further separated and purified by repeated preparative TLC.

† The rank of *Dermocybe* remains a matter for debate. Consistent with most recent chemical publications[10] and in line with Moser[11] we have elected to treat *Dermocybe* as a genus. Other authorities regard *Dermocybe* as a subgenus of *Cortinarius*.

Table 1. ^{1}H NMR chemical shifts and coupling constants for quinones (**6**), (**8**), and (**10**) (δ ppm relative to Me_4Si $CDCl_3$).[a]

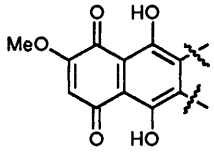
Proton	(6)	(8)	(10)
1-H	5.21 (m)	5.08 (m)	5.18 (m)
2-H_a	1.89 (dd, 14.7, 5.1)	1.82 (dd, 14.7, 5.1)	1.74 (dd, 13.6, 9.2)
2-H_e	2.35 (ddd, 14.7, 1.8, 1.8)	2.30 (ddd, 14.7, 1.8, 1.8)	2.31 (ddd, 13.6, 6.6, 2.6)
3-Me	1.48 (s)	1.45 (s)	1.47 (s)
4-H_a	2.54 (d, 19.1)	2.41 (dd, 19.8, 1.5)	2.55 (dd, 19.4, 2.9)
4-H_e	3.19 (dd, 19.1, 1.8)	3.02 (dd, 19.8, 1.8)	2.80 (ddd, 19.4, 2.6, 1.8)
5-H	—	7.19 (d, 2.6)	7.17 (d, 2.6)
6-OMe	3.95 (s)	3.91 (s)	3.91 (s)
7-H	6.20 (s)	6.65 (d, 2.6)	6.62 (d, 2.6)
1-OH	3.63 (br s)	3.51 (d, 5.1)	4.00 (d, 2.2)
3-OH	3.26 (br s)	3.06 (s)	—
peri-OH	12.69 (s) 13.32 (s)	12.21 (s)	12.15 (s)

[a] Assignments corroborated by consecutive selective irradiations of the aliphatic protons in ^{1}H-{^{1}H} homonuclear decoupling experiments.

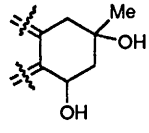


(**12**) R^1 = OH, R^2 = H
(**13**) R^1 = R^2 = H
(**14**) R^1 = OAc, R^2 = Ac
(**15**) R^1 = H, R^2 = Ac

The principal pigment (**6**),* $C_{16}H_{16}O_7$ (mass spectrometry and combustion analysis), which we have called austrocortirubin, was obtained as dark red needles, m.p. 193–195 °C after crystallisation from benzene–light petroleum (b.p. 60–80 °C) in a yield corresponding to 4.1 × 10^{-2}% of the fresh weight of the fungus. The pigment is optically active, $[\alpha]_D^{20}$ + 34° (*c* 0.543 in $CHCl_3$), and from its electronic and IR spectra was identified as a naphthazarin derivative.[14] In the mass spectrum austrocortirubin loses two molecules of water from a molecular ion at *m/z* 320 to give the base peak in the spectrum at *m/z* 284. In the ^{1}H NMR spectrum austrocortirubin shows a methoxyl resonance at δ 3.95 and singlets at δ 6.20, 12.69, and 13.32 which were assigned to a quinonoid methine proton and two chelated phenolic hydroxy groups, respectively, consistent with a naphthazarin substructure of the type (**16**). The remaining ten



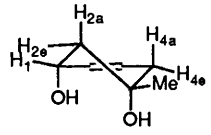
(**16**)



(**17**)

protons in the ^{1}H NMR spectrum resonate at lower frequency and form a couplet (Table 1) which may be interpreted unequivocally after selective decoupling in terms of the 1,3-dihydroxy-3-methyl-1,2,3,4-tetrahydro-aromatic substructure (**17**).

Furthermore, the magnitude of the vicinal coupling constants ($J \leqslant 5.1$ Hz) between the alcoholic methine proton (1-H) and the methylene protons at C-2 at once precludes any *trans*-diaxial relationship and places the hydroxy group at C-1 in an axial configuration. Similarly, other couplings within the tetrahydroaromatic ring in structure (**6**), in particular the observation of long range 'w' coupling between the equatorial protons of the C-2 and C-4 methylene groups, lead to the conclusion that the half chair conformation (**18**) is preferred.



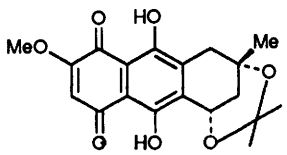
(**18**)

Having rationalised the molecular formula of austrocortirubin in terms of partial structures (**16**) and (**17**) the connectivity between these subunits was then established by chemical correlation with the diacetyl derivative (**14**) of 1,4-dihydroxy-2-methoxy-7-methyl-9,10-anthraquinone (austrocortinin) (**12**).[12,15] Accordingly, austrocortirubin (**6**) was treated with acetic anhydride in the presence of a trace of concentrated sulphuric acid whereupon the known diacetate (**14**), m.p. 241–246 °C (lit.,[15] 242–248 °C) was obtained. The diacetate (**14**) is readily distinguished by high field ^{1}H NMR spectroscopy from its regioisomer, 1,4-dihydroxy-2-methoxy-6-methyl-9,10-anthraquinone,[16] the absence of which precludes the alternative connectivity between substructures (**16**) and (**17**) in austrocortirubin.

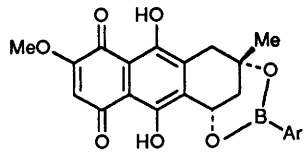
The relative configuration of the hydroxy groups in the tetrahydroaromatic ring in compound (**6**) was established as *cis* by smooth formation of the acetonide derivative (**19**), $C_{19}H_{20}O_7$, m.p. 264–268 °C, $[\alpha]_D^{20}$ + 189° (*c* 0.308 in $CHCl_3$), on treatment of austrocortirubin with 2,2-dimethoxypropane in the presence of a trace of *p*-toluenesulphonic acid. Similarly, treatment of compound (**6**) with phenyl- and with *p*-bromophenylboronic acid gave the boronate esters (**20**) and (**21**), respectively, under mild conditions and in high yields. A close correspondence between the chemical shifts and coupling constants of protons in the tetrahydroaromatic rings in the derivatives (**19**)–(**21**) and those of the parent quinone (**6**) reveals that no fundamental change in conformation had taken place during derivatisation thereby adding support to the proposition that austrocortirubin in solution occupies the half chair conformation depicted in partial structure (**18**).

Austrocortirubin and its derivatives, like other naphthazarins might be expected to exist in solution as mixtures of quinonoid

* IUPAC nomenclature rules dictate that in numbering the nucleus of the quinone (**6**) the left hand ring should take priority. However, for consistency and comparison between spectroscopic data we have numbered quinone (**6**) and its derivatives in the same way as shown in the formula for quinone (**8**). The numbering in quinones (**8**) and (**10**) is in accord with IUPAC recommendations.



(19)



(20) Ar = Ph
(21) Ar = 4-BrC_6H_4

tautomers. However, comparison of the chemical shifts in deuteriochloroform of the 7-H resonance in the ^{1}H NMR spectra of compounds (**6**) (δ 6.20), (**19**) (δ 6.20), (**20**) (δ 6.19), and (**21**) (δ 6.19) with the shifts of analogous protons located in benzenoid (typically δ 6.6–6.7) and in quinonoid (typically δ 6.1–6.2) rings in a range of 2-alkoxynaphthazarins[16,17] strongly suggests that these pigments exist in solution predominantly as the tautomers shown. This suggestion is corroborated by the fully proton-coupled ^{13}C NMR spectrum of compound (**6**) in which one carbonyl carbon atom (C-5) appears as a doublet (*J* 7.4 Hz) which on simultaneous irradiation at the resonance frequency of the C-7 proton (δ 6.20) collapses to a singlet (δ 178.3). The remainder of the ^{13}C NMR spectrum of austrocortirubin (see **Experimental**) is fully consistent with the assigned structure.

That the tautomeric form depicted in formulae (**6**) and (**19**)–(**21**) is also preferred in the solid state was established from a single crystal X-ray analysis of the phenylboronate ester (**20**) of austrocortirubin. The result of this structure determination is fully consistent with the stoicheiometry and connectivity implied by formula (**20**). Figure 1 is a view of the molecular structure which clearly shows that this quinone, like bostrycin (**4**),[16] prefers that tautomeric form in which the quinone moiety occupies the peripheral ring in the tetrahydroanthraquinone nucleus.

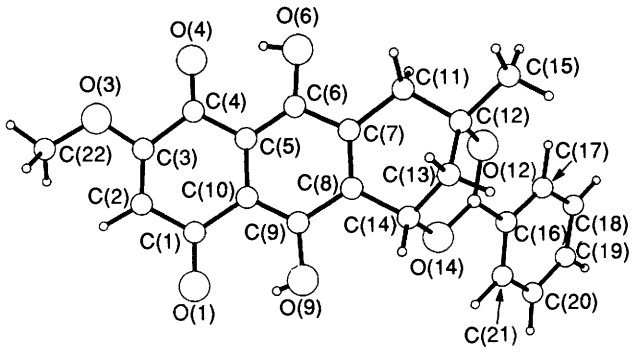
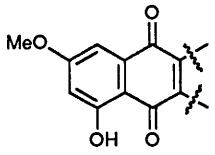


Figure 1. Molecular structure of compound (**20**).

The principal yellow pigment (**8**), $C_{16}H_{16}O_6$ (mass spectrometry and combustion analysis), which we have called austrocortilutein, was obtained as orange-yellow needles, m.p. 183–185 °C after crystallisation from chloroform–light petroleum (b.p. 60–80 °C) in a yield corresponding to 2.2 × 10^{-2}% of the fresh weight of the fungus. Like austrocortirubin (**6**), austrocortilutein (**8**) is strongly dextrorotatory {$[\alpha]_D^{20}$ + 52° (*c* 0.095 in $CHCl_3$)}.

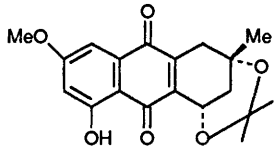
Austrocortilutein exhibits an ^{1}H NMR spectrum in which a pair of *meta*-coupled aromatic resonances (δ 6.65 and 7.19) and a single low field signal (δ 12.21) replace the quinonoid proton singlet and the two hydroxyl resonances, respectively, in the spectrum of austrocortirubin (**6**). This, together with the electronic spectrum, is indicative of the 5-hydroxy-1,4-naphthoquinone subunit (**22**). Signals in the aliphatic proton region in the ^{1}H NMR spectrum of austrocortilutein (Table 1) reveal the same dihydroxylated tetrahydroaromatic ring (**17**) occupying a similar half chair conformation (**18**) to that present in austrocortirubin (**6**).



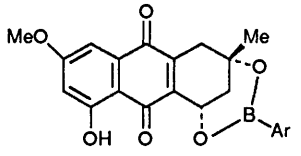
(22)

As before, connectivity between the chromophore (**22**) and the substructure (**17**) in austrocortilutein (**8**) was established by treatment of the pigment with acetic anhydride in the presence of a trace of concentrated sulphuric acid. Under these conditions the sole product was the crystalline acetate (**15**), m.p. 171–173 °C (lit.,[18] 171–173 °C), of the ether (**13**) which proved indistinguishable from an authentic sample derived from *Alternaria solani*.[18]

Treatment of austrocortilutein with 2,2-dimethoxypropane afforded the acetonide (**23**), $C_{19}H_{20}O_6$, m.p. 192–195 °C, as yellow needles from chloroform–light petroleum (b.p. 60–80 °C), $[\alpha]_D^{20}$ + 60° (*c* 0.297 in $CHCl_3$). This, together with smooth formation of the arylboronate esters (**24**) and (**25**) on exposure of austrocortilutein to phenyl- and *p*-bromophenylboronic acid, respectively, established the mutual *cis* relationship between the hydroxy groups occupying the stereocentres in austrocortilutein (**8**).



(23)



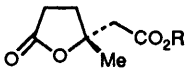
(24) Ar = Ph
(25) Ar = 4 - BrC_6H_4

Having established the gross structures and relative stereochemistry of austrocortirubin (**6**) and austrocortilutein (**8**) we next turned our attention to the absolute stereochemistry of these compounds. Since neither of the *p*-bromophenylboronate esters (**21**) or (**25**) afforded crystals suitable for X-ray analysis we pursued a chemical solution to this problem.

A cursory examination of the disposition of hydroxy groups in the tetrahydroaromatic ring in compound (**6**) reveals that any attempt to excise the chiral centres (*e.g.*, by ozonolysis followed by periodate cleavage) from austrocortirubin itself would lead to an aliphatic fragment, 3-hydroxy-3-methylglutaric acid, in which all stereochemical information pertaining to the parent quinone would be lost. On the other hand, removal of the benzylic hydroxy group in compound (**6**) prior to oxidative degradation should lead to 3-hydroxy-3-methyladipic acid containing the chiral centre excised from C-3 in austrocortirubin. Since the relative stereochemistry between C-1 and C-3 in compound (**6**) is already established such a sequence should reveal the absolute stereochemistry at both chiral centres in austrocortirubin (**6**).

Accordingly, catalytic hydrogenolysis of austrocortirubin in methanol gave 1-deoxyaustrocortirubin (**7**), m.p. 211–216 °C, $[\alpha]_D^{20}$ − 59° (*c* 0.049 in $CHCl_3$), as the major product (>80% yield). An orange by product (5%) was subsequently identified with the deoxy derivative (**9**) of austrocortilutein (**8**) (see below). Treatment of (−)-1-deoxyaustrocortirubin (**7**) under a variety

of reaction conditions with ozone followed by sodium periodate failed to yield identifiable products. However, with ruthenium tetraoxide, generated *in situ* from ruthenium trichloride and sodium metaperiodate in a heterogenous mixture of carbon tetrachloride, acetonitrile and water,[19] the quinone (**7**) afforded a mixture of products in which the carboxylic acid (**26**) could be detected by TLC. Methylation of acid (**26**) without prior purification gave the ester (**27**), $[\alpha]_D^{20}$ + 9.8° (*c* 2.19 in $CHCl_3$)



(**26**) R = H
(**27**) R = Me

in 45% yield from austrocortirubin itself. The absolute configuration of the ester (**27**) was determined by direct comparison of specific rotation of the naturally derived material with that of (2*R*)-methyl 2-(2′-methyl-5′-oxofuryl)acetate, $[\alpha]_D^{20}$ + 10.3° (*c* 2.39 in $CHCl_3$), a new compound prepared by us for this purpose *via* Sharpless asymmetric epoxidation from geraniol.[20] It follows that the absolute configuration of (−)-1-deoxyaustrocortirubin (**7**) must be (3*R*) and consequently that of austrocortirubin itself must be (1*S*,3*S*), as depicted in formula (**6**).

An analogous sequence of reactions led from the principal yellow pigment (**8**), *via* its 1-deoxy derivative (**9**), m.p. 206–212 °C, $[\alpha]_D^{20}$ − 78° (*c* 0.051 in $CHCl_3$), to the (*R*)-ester (**27**), $[\alpha]_D^{20}$ + 9.8° (*c* 2.05 in $CHCl_3$). Thus, (−)-1-deoxyaustrocortilutein (**9**) and consequently austrocortilutein (**8**) itself must possess (3*R*) and (1*S*,3*S*) configurations, respectively, as depicted in their molecular formulae.

The laevorotatory 1-deoxy derivatives (**7**) and (**9**) of austrocortirubin and austrocortilutein have been reported previously as minor constituents of *D. splendida*.[13] The stereochemical studies detailed here now establish the absolute configuration of both these naturally occurring quinones as (3*R*).

Although we were unable to obtain crystals of either of the *p*-bromophenylboronates (**21**) or (**25**) suitable for X-ray analysis we have carried out a successful single crystal structure determination of the acetonide (**23**) of austrocortilutein. By including the small anomalous scattering of the six oxygen atoms in the structure factor calculations it has proved possible to assign the (1*S*,3*S*) configuration to acetonide (**23**) and thereby to confirm the (1*S*,3*S*) absolute stereochemistry for austrocortilutein (**8**).

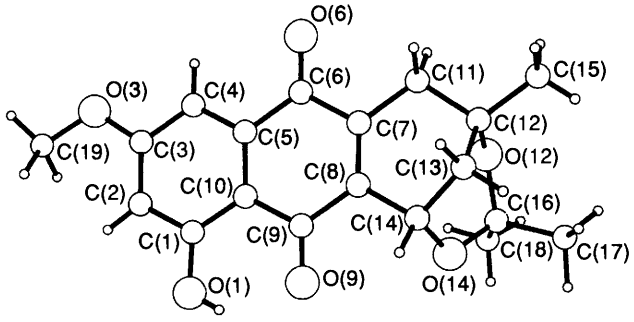
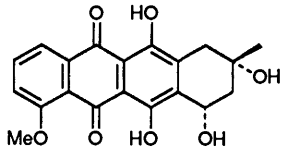


Figure 2. Molecular structure of compound (**23**).

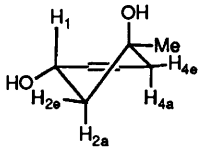
The result of this structure determination is fully consistent with the stoicheiometry and connectivity implied in formula (**23**) and, taken together with anomalous scattering and other crystallographic evidence detailed fully below indicates the absolute configuration shown in Figure 2 to be correct. Since austrocortirubin (**6**) and austrocortilutein (**8**) have been correlated chemically at the level of the 1-deoxy derivative (**9**) (see above) this X-ray analysis also indirectly corroborates the deduction of (1*S*,3*S*) stereochemistry for austrocortirubin.

The pigments (**6**) and (**8**) are the first naturally occurring tetrahydroanthraquinones which possess a *cis*-1,3 arrangement of hydroxy groups in the hydroaromatic ring. Thus, they differ in relative stereochemistry from altersolanol-A (**1**) and bostrycin (**4**), the only two known tetrahydroanthraquinones with a hydroxy group both at C-1 and C-3, and correspond more closely both in relative and absolute stereochemical terms to the anthracyclinone class of antitumour antibiotics, *e.g.*, feudomycinone-C (**28**).[21]



(**28**)

A minor yellow pigment present in the extracts of *D. splendida* and intermediate in R_F between austrocortirubin (**6**) and (1*S*,3*S*)-austrocortilutein (**8**) was isolated after preparative TLC as yellow needles, m.p. 162–164 °C, $[\alpha]_D^{20}$ + 288° (*c* 0.100 in $CHCl_3$), in a yield of 1.5 × 10^{-3}% of the fresh weight of the fungus. The mass spectrum and combustion analysis data led to the molecular formula $C_{16}H_{16}O_6$ and thereby identified this metabolite as an isomer of the major yellow pigment (**8**). Treatment of the minor pigment with acetic anhydride in the presence of a trace of concentrated sulphuric acid gave the acetate (**15**) which had previously been isolated on similar treatment from (1*S*,3*S*)-austrocortilutein. This, together with the near identity between the UV and ^1H NMR (δ > 5) spectra of the two yellow metabolites inferred that the pigments are diastereoisomers. This suggestion found further support in the aliphatic proton region of the ^1H NMR spectrum of the minor metabolite (Table 1) wherein one may readily discern signals consistent with the partial structure (**17**). However, on this occasion the chemical shifts and coupling constants are best rationalised in terms of the half chair conformation (**29**) in



(**29**)

which the hydroxy groups at C-1 and C-3 are mutually *trans* disposed. Of particular significance in this regard is the observation of a 9.2 Hz coupling between the benzylic methine proton (1-H) and the axial proton of the methylene group at C-2, which clearly implies a *trans*-diaxial relationship and places the hydroxy group at C-1 in an equatorial configuration. In turn, the similar chemical shift exhibited by the C-methyl group in the spectra of the major (δ 1.45) and minor (δ 1.47) yellow pigments suggests that in both molecules this group occupies an equatorial configuration, a conclusion which places the C-3 hydroxyl axial and consequently on the opposite mean face of the tetrahydroaromatic ring to the benzylic hydroxy group in the minor metabolite. Thus, the *trans*-diol structure (**10**) may be assigned to the minor yellow pigment. In accord with this relative stereochemistry the pigment (**10**) does not react either with 2,2-dimethoxypropane or with phenylboronic acid.

The absolute configuration of the pigment (**10**) was established by hydrogenolysis of the benzylic hydroxy group whereupon the sole product was 1-deoxyaustrocortilutein (**11**), m.p. 206–211 °C, $[\alpha]_D^{20}$ + 73° (*c* 0.060 in $CHCl_3$). Comparison of

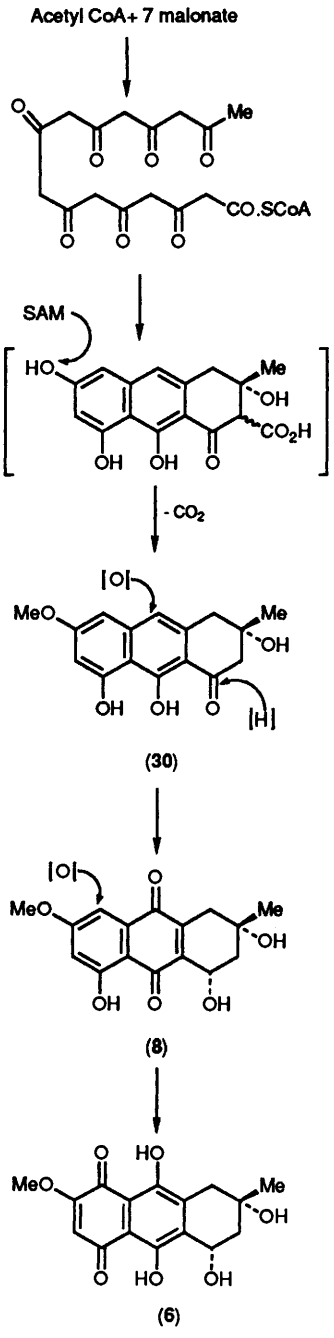
the specific rotation of this product with that of the (3*R*)-quinone (**9**), which had in turn been correlated with the (*R*)-ester (**27**), establishes (3*S*) stereochemistry for (**11**) and hence the (1*S*,3*R*) configuration for the minor pigment (**10**). To avoid an unnecessary proliferation of trivial names we prefer to use the name (1*S*,3*R*)-austrocortilutein for pigment (**10**).

It is notable that the tetrahydroaromatic ring in pigment (**10**) assumes the conformation (**29**) in which the C-3 methyl group is maintained in an equatorial configuration necessitating a similar orientation for the hydroxy group at C-1. The conformation of compound (**10**) therefore represents the alternative half chair to that preferred by (1*S*,3*S*)-austrocortilutein (**8**).

The tetrahydroanthraquinones (**6**), (**8**), and (**10**) are effective at low concentrations in the growth inhibition of a variety of bacteria and fungi. Austrocortirubin (**6**), for example, is active in the plate diffusion assay (6 mm discs) at 10 μg per disc against the following micro-organisms (zone of inhibition in mm is given in parentheses): *Bacillus brevis* (32), *B. subtilis* (29), *Mucor miehei* (29), *Penicillium notatum* (20), and *Nematospora coryli* (21),[22] It is notable that the extent of inhibition by austrocortirubin (**6**) did not diminish markedly on increasing the dilution to 2 μg per disc. The austrocortilutein stereoisomers (**8**) and (**10**), and 1-deoxyaustrocortirubin (**7**) showed significant but nevertheless somewhat reduced activities compared to austrocortirubin against the same array of micro-organisms whereas the deoxy derivative (**9**) exhibited practically no inhibitory activity in the same assays.

Our isolation of the pigments (**6**), (**8**), and (**10**) together with our earlier report[13] of the deoxy compounds (**7**) and (**9**) from *Dermocybe splendida* brings the total number of naturally occurring tetrahydroanthraquinones from five to ten. Their presence in the higher fungi, particularly in toadstools belonging to the genus *Dermocybe* is of taxonomic significance[9] when it is taken into account that anthraquinones proper have come to occupy an important position in the differentiation of infrageneric taxa among Northern Hemisphere species of *Dermocybe, Cortinarius* and their allies.[23] Significant in the same regard is our failure to detect any of the many familiar *Cortinarius* anthraquinones in *Dermocybe splendida*.[12]

Despite a divergence in detail, the structures of the tetrahydroanthraquinones from *D. splendida* betray a close biosynthetic relationship with the many anthraquinone and pre-anthraquinone pigments which have been isolated from the Cortinareaceae.[10] In view of our recent isolation of (3*S*)-torosachrysone (**30**) from fruit bodies of *D. splendida* and our establishment of an octaketide origin for this metabolite in several related species[24] it seems reasonable to suggest a pathway, outlined in the Scheme, by which the principal pigments (**6**) and (**8**) may arise *via* the pivotal intermediate (**30**).



Scheme. Possible biosynthesis of austrocortirubin (**6**) and austrocortilutein (**8**).

Crystallographic Analysis of Austrocortirubin Phenylboronate (**20**) *and Austrocortilutein Acetonide* (**23**).—Compound (**20**): $C_{22}H_{19}O_7B$, M = 406.19, orthorhombic, a = 7.011 (1), b = 16.670(2), c = 33.670(4) Å, V = 3 935.0 Å^3, Z = 8, D_c = 1.37 g cm^{-3}, $F(000)$ = 1 696, space group $P2_12_12_1$, Cu-K_α radiation λ = 1.541 78 Å, μ(Cu-K_α) = 8.6 cm^{-1}.

Compound (**23**): $C_{19}H_{20}O_6$, M = 344.37, orthorhombic, a = 7.254(1), b = 12.434(1), c = 18.511(1) Å, V = 1 669.6 Å^3, Z = 4, D_c = 1.37 g cm^{-3}, $F(000)$ = 728, space group $P2_12_12_1$, Cu-K_α radiation λ = 1.541 78 Å, μ (Cu-K_α) = 8.6 cm^{-1}.

Crystals of approximate dimensions 0.6 × 0.5 × 0.2 mm for compound (**23**) and 0.5 × 0.15 × 0.01 mm for compound (**20**) were mounted on an Enraf-Nonius CAD 4 diffractometer and 25 reflections were used to determine accurate lattice parameters by least squares. Intensity data were collected for 1° < θ < 76° for compound (**23**) but only out to 60° for compound (**20**) whose small crystal size gave only weak diffraction maxima. Totals of 2 007 [(**23**)] and 3 351 [(**20**)] independent reflections were measured of which 1 730 and only 1 094, respectively, were considered observed with $I > 3\sigma(I)$ [(**23**)] and $I > 2\sigma(I)$ [(**20**)] and used in the subsequent refinement. The data for compound (**20**) were collected very slowly to achieve even this level of observed intensities. The data were corrected for Lorentz and polarisation factors but no absorption corrections were made. Crystallographic calculations were performed using the CRYSTALS system of programs.[25] The structures were solved by direct methods using the MULTAN program.[26] The structure of compound (**20**) with two crystallographically independent molecules as the asymmetric unit and very weak diffraction data was only solved after many trial attempts. Eventually the data was renormalised in two zones <35° and >35°. In the outer zone E values for well

Table 2. Fractional atomic co-ordinates with standard deviations in parentheses for compound (**20**).

Atom	*x/a*	*y/b*	*z/c*
C(1)	0.217(3)	0.638(1)	0.210 7(5)
C(2)	0.262(3)	0.654(1)	0.169 0(4)
C(3)	0.283(3)	0.729(1)	0.157 6(5)
C(4)	0.266(3)	0.800(1)	0.182 8(5)
C(5)	0.217(2)	0.785 0(9)	0.223 9(4)
C(6)	0.193(3)	0.847(1)	0.248 9(5)
C(7)	0.134(3)	0.837(1)	0.289 5(5)
C(8)	0.102(2)	0.760 8(9)	0.303 4(4)
C(9)	0.133(3)	0.694(1)	0.276 3(5)
C(10)	0.189(3)	0.706 8(9)	0.237 5(4)
C(11)	0.100(3)	0.911(1)	0.315 3(5)
C(12)	0.038(3)	0.890(1)	0.358 1(5)
C(13)	−0.076(3)	0.812(1)	0.360 5(5)
C(14)	0.039(3)	0.745(1)	0.345 3(5)
C(15)	−0.061(3)	0.963(1)	0.378 0(5)
C(16)	0.456(2)	0.792(1)	0.416 6(5)
C(17)	0.531(3)	0.859(1)	0.434 8(5)
C(18)	0.679(4)	0.854(1)	0.463 8(6)
C(19)	0.746(3)	0.779(1)	0.472 4(5)
C(20)	0.676(3)	0.711(1)	0.456 0(5)
C(21)	0.524(3)	0.718(1)	0.427 4(5)
C(22)	0.343(3)	0.688(1)	0.090 8(6)
O(1)	0.195(2)	0.566 7(7)	0.222 6(3)
O(3)	0.327(2)	0.750 5(7)	0.118 9(4)
O(4)	0.298(2)	0.869 4(7)	0.169 8(3)
O(6)	0.218(2)	0.925 2(7)	0.238 5(3)
O(9)	0.110(2)	0.620 3(7)	0.291 7(3)
O(12)	0.216(2)	0.876 6(6)	0.379 9(3)
O(14)	0.206(2)	0.735 2(6)	0.370 5(3)
B(1)	0.286(3)	0.802(1)	0.387 2(5)
C(31)	0.276(3)	0.153(1)	0.301 8(5)
C(32)	0.324(3)	0.138(1)	0.260 7(5)
C(33)	0.342(3)	0.203(1)	0.238 3(5)
C(34)	0.329(3)	0.286(1)	0.250 4(5)
C(35)	0.273(3)	0.297 4(9)	0.292 2(4)
C(36)	0.240(3)	0.373 6(9)	0.307 6(4)
C(37)	0.175(3)	0.388(1)	0.347 4(4)
C(38)	0.153(3)	0.323 0(9)	0.371 5(5)
C(39)	0.195(2)	0.246(1)	0.356 6(4)
C(40)	0.245(3)	0.232(1)	0.317 8(4)
C(41)	0.141(3)	0.474(1)	0.359 5(5)
C(42)	0.088(3)	0.479(1)	0.403 8(5)
C(43)	−0.035(3)	0.409(1)	0.416 2(5)
C(44)	0.079(3)	0.334(1)	0.413 2(5)
C(45)	0.004(3)	0.561(1)	0.412 7(5)
C(46)	0.486(3)	0.418(1)	0.475 7(5)
C(47)	0.571(3)	0.353(1)	0.496 8(5)
C(48)	0.711(3)	0.364(1)	0.523 4(5)
C(49)	0.772(4)	0.441(1)	0.533 2(6)
C(50)	0.697(3)	0.505(1)	0.514 0(6)
C(51)	0.556(3)	0.494(1)	0.486 7(5)
C(52)	0.415(3)	0.120(1)	0.182 4(5)
O(31)	0.260(2)	0.092 6(7)	0.326 0(3)
O(33)	0.386(2)	0.197 5(8)	0.198 5(4)
O(34)	0.348(2)	0.341 9(8)	0.227 4(3)
O(36)	0.270(2)	0.440 9(7)	0.284 9(3)
O(39)	0.164(2)	0.184 0(7)	0.382 3(3)
O(42)	0.265(2)	0.477 5(7)	0.426 9(3)
O(44)	0.241(2)	0.336 2(7)	0.440 5(3)
B(31)	0.320(4)	0.411(1)	0.444 7(7)

observed reflections were estimated manually at sufficiently large values to allow them to play their proper major role in the phase determination process. The very large number of unobserved reflections in this range meant that the *E* values originally calculated for these reflections were much too low.[27] In this way 157 calculated *E* values for reflections with $\theta < 35°$ were combined with 205 estimated *E* values for reflections with $\theta > 35°$ and input to the MULTAN program. The resulting set of phases enabled the successful location of 41 of the 60 non-hydrogen atoms in the structure. The remaining atoms were located by Fourier methods.

Table 3. Bond lengths (Å) with standard deviations in parentheses for compound (**20**).

	mol(A)	mol(B)
C(1)–C(2)	1.46(2)	1.44(2)
C(1)–C(10)	1.47(2)	1.44(2)
C(1)–O(1)	1.27(2)	1.30(2)
C(2)–C(3)	1.31(2)	1.33(2)
C(3)–C(4)	1.46(2)	1.43(2)
C(3)–O(3)	1.39(2)	1.38(2)
C(4)–C(5)	1.45(2)	1.48(2)
C(4)–O(4)	1.26(2)	1.22(2)
C(5)–C(6)	1.35(2)	1.39(2)
C(5)–C(10)	1.39(2)	1.40(2)
C(6)–C(7)	1.44(2)	1.43(2)
C(6)–O(6)	1.36(2)	1.37(2)
C(7)–C(8)	1.37(2)	1.36(2)
C(7)–C(11)	1.54(2)	1.51(2)
C(8)–C(9)	1.46(2)	1.42(2)
C(8)–C(14)	1.50(2)	1.51(2)
C(9)–C(10)	1.38(2)	1.37(2)
C(9)–O(9)	1.34(2)	1.36(2)
C(11)–C(12)	1.55(2)	1.54(2)
C(12)–C(13)	1.52(2)	1.51(2)
C(12)–C(15)	1.55(2)	1.52(2)
C(12)–O(12)	1.46(2)	1.46(2)
C(13)–C(14)	1.48(2)	1.48(2)
C(14)–O(14)	1.45(2)	1.46(2)
C(16)–C(17)	1.38(2)	1.43(2)
C(16)–C(21)	1.38(2)	1.40(2)
C(16)–B(1)	1.55(3)	1.57(3)
C(17)–C(18)	1.42(3)	1.34(3)
C(18)–C(19)	1.38(2)	1.39(3)
C(19)–C(20)	1.35(2)	1.35(3)
C(20)–C(21)	1.45(2)	1.36(3)
C(22)–O(3)	1.42(2)	1.42(2)
O(12)–B(1)	1.36(2)	1.32(2)
O(14)–B(1)	1.36(2)	1.37(2)

Least-squares refinement including anisotropic thermal parameters for non-hydrogen atoms and isotropic refinement of hydrogen atoms located in a difference Fourier synthesis terminated at *R* 0.0372 (R_w 0.0401) for compound (**23**). The much weaker data for compound (**20**) only allowed isotropic refinement of non-hydrogen atoms and inclusion of the hydrogen atoms in calculated positions, without refinement, following their approximate location in a difference Fourier synthesis, and terminated at *R* 0.0613 (R_w 0.0703). Final difference maps showed no features in excess of 0.2 e Å^{-3} for either structure.

The refined fractional atomic co-ordinates are shown in Tables 2 and 5 and the resulting bond lengths and bond angles are displayed in Tables 3, 4, 6, and 7. These do not differ significantly from expected values, after allowance is made for the larger standard deviations in compound (**20**). Figures 1 and 2 are views of the molecular structures of compounds (**20**) and (**23**), respectively. They show the atom labelling scheme employed in the refinement of the structures. The numbering is not in line with the IUPAC recommendations according to which the heterocyclic ring should take precedence in each case. Thermal parameters and hydrogen atom positions have been deposited at the Cambridge Crystallographic Data Centre.*

* For details of the supplementary publications scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1990, in the January issue.

Table 4. Bond angles (°) with standard deviations in parentheses for compound (**20**).

	mol(A)	mol(B)
C(2)–C(1)–C(10)	119(1)	124(2)
C(2)–C(1)–O(1)	120(2)	119(2)
C(10)–C(1)–O(1)	121(1)	117(2)
C(1)–C(2)–C(3)	118(2)	115(2)
C(2)–C(3)–C(4)	126(2)	128(2)
C(2)–C(3)–O(3)	123(2)	121(2)
C(4)–C(3)–O(3)	111(1)	111(2)
C(3)–C(4)–C(5)	116(2)	115(2)
C(3)–C(4)–O(4)	122(1)	123(2)
C(5)–C(4)–O(4)	122(2)	122(2)
C(4)–C(5)–C(6)	120(2)	121(1)
C(4)–C(5)–C(10)	121(1)	121(2)
C(6)–C(5)–C(10)	120(1)	117(1)
C(5)–C(6)–C(7)	122(2)	123(2)
C(5)–C(6)–O(6)	124(2)	121(1)
C(7)–C(6)–O(6)	114(1)	116(1)
C(6)–C(7)–C(8)	119(1)	118(2)
C(6)–C(7)–C(11)	119(1)	117(1)
C(8)–C(7)–C(11)	122(1)	125(1)
C(7)–C(8)–C(9)	118(1)	119(2)
C(7)–C(8)–C(14)	122(2)	120(2)
C(9)–C(8)–C(14)	120(2)	121(1)
C(8)–C(9)–C(10)	121(2)	123(2)
C(8)–C(9)–O(9)	116(1)	115(1)
C(10)–C(9)–O(9)	123(2)	122(2)
C(1)–C(10)–C(5)	120(1)	117(2)
C(1)–C(10)–C(9)	120(2)	123(2)
C(5)–C(10)–C(9)	120(2)	120(2)
C(7)–C(11)–C(12)	113(1)	111(1)
C(11)–C(12)–C(13)	113(1)	111(2)
C(11)–C(12)–C(15)	110(2)	109(2)
C(11)–C(12)–O(12)	105(1)	108(1)
C(13)–C(12)–C(15)	114(2)	115(2)
C(13)–C(12)–O(12)	107(1)	109(1)
C(15)–C(12)–O(12)	106(1)	104(1)
C(12)–C(13)–C(14)	110(1)	109(2)
C(8)–C(14)–C(13)	110(1)	111(1)
C(8)–C(14)–O(14)	109(1)	109(1)
C(13)–C(14)–O(14)	109(1)	111(1)
C(17)–C(16)–C(21)	119(2)	114(2)
C(17)–C(16)–B(1)	120(2)	125(2)
C(21)–C(16)–B(1)	121(2)	120(2)
C(16)–C(17)–C(18)	123(2)	122(2)
C(17)–C(18)–C(19)	116(2)	120(2)
C(18)–C(19)–C(20)	124(2)	120(2)
C(19)–C(20)–C(21)	118(2)	120(2)
C(16)–C(21)–C(20)	120(2)	123(2)
C(3)–O(3)–C(22)	117(1)	118(2)
C(12)–O(12)–B(1)	122(1)	120(2)
C(14)–O(14)–B(1)	119(1)	114(1)
C(16)–B(1)–O(12)	119(2)	117(2)
C(16)–B(1)–O(14)	120(2)	116(2)
O(12)–B(1)–O(14)	121(2)	127(2)

The absolute configuration of compound (**23**) was investigated by including the small anomalous scattering of the six oxygen atoms in the structure factor calculations. *R* values of 0.038 420 and 0.038 636 were obtained for the two different inverted configurations respectively. This gives an *R* factor ratio $\mathscr{R}$ 1.0056 ($\mathscr{R}_w$ 1.0017), for the one dimensional hypothesis with 1 423 degrees of freedom. These small values are nevertheless significant at the 97.5% level and indicate the absolute configuration shown in Figure 2 to be correct.[28] Similar calculations for the weaker data of compound (**20**) gave corresponding *R* values of 0.061 467 and 0.061 644. This gives an *R* factor ratio $\mathscr{R}$ 1.0029 ($\mathscr{R}_w$ 1.0011) for the one dimensional hypothesis with only 852 degrees of freedom. Although much less significant at only the 90% level they do indicate an identical absolute configuration.

Table 5. Fractional atomic co-ordinates with standard deviations in parentheses for compound (**23**).

Atom	*x/a*	*y/b*	*z/c*
C(1)	0.227 7(4)	0.057 1(2)	0.551 8(1)
C(2)	0.243 0(5)	0.072 6(2)	0.477 1(1)
C(3)	0.265 2(5)	0.174 5(2)	0.450 9(1)
C(4)	0.276 4(5)	0.263 8(2)	0.497 3(2)
C(5)	0.261 8(4)	0.248 3(2)	0.570 6(1)
C(6)	0.272 9(5)	0.342 9(2)	0.619 3(1)
C(7)	0.257 2(4)	0.323 8(2)	0.698 9(1)
C(8)	0.224 0(4)	0.225 0(2)	0.724 8(1)
C(9)	0.213 2(4)	0.130 0(2)	0.677 0(1)
C(10)	0.235 6(4)	0.145 2(2)	0.599 2(1)
C(11)	0.279 2(5)	0.421 5(2)	0.746 4(1)
C(12)	0.296 1(4)	0.389 8(2)	0.826 3(1)
C(13)	0.140 9(5)	0.309 7(3)	0.842 0(2)
C(14)	0.192 7(4)	0.205 7(2)	0.805 1(2)
C(15)	0.295 1(6)	0.488 3(3)	0.875 0(2)
C(16)	0.488 0(5)	0.234 4(2)	0.865 3(2)
C(17)	0.467 9(6)	0.244 3(3)	0.947 8(2)
C(18)	0.674 6(5)	0.192 2(3)	0.845 5(2)
C(19)	0.272 7(7)	0.111 6(3)	0.329 0(2)
O(1)	0.205 3(4)	−0.043 8(2)	0.575 0(1)
O(3)	0.279 1(5)	0.199 2(2)	0.379 5(1)
O(6)	0.292 0(4)	0.433 3(2)	0.596 1(1)
O(9)	0.184 7(4)	0.039 8(2)	0.703 1(1)
O(12)	0.473 4(3)	0.335 9(2)	0.830 2(1)
O(14)	0.354 9(3)	0.159 1(2)	0.837 9(1)

Table 6. Bond lengths (Å) with standard deviations in parentheses for compound (**23**).

C(1)–C(2)	1.401(3)
C(1)–C(10)	1.404(4)
C(1)–O(1)	1.336(3)
C(2)–C(3)	1.366(4)
C(3)–C(4)	1.405(4)
C(3)–O(3)	1.360(3)
C(4)–C(5)	1.375(4)
C(5)–C(6)	1.484(4)
C(5)–C(10)	1.401(3)
C(6)–C(7)	1.497(4)
C(6)–O(6)	1.211(3)
C(7)–C(8)	1.340(3)
C(7)–C(11)	1.508(4)
C(8)–C(9)	1.478(4)
C(8)–C(14)	1.523(4)
C(9)–C(10)	1.462(3)
C(9)–O(9)	1.239(3)
C(11)–C(12)	1.535(4)
C(12)–C(13)	1.531(4)
C(12)–C(15)	1.520(5)
C(12)–O(12)	1.452(3)
C(13)–C(14)	1.511(4)
C(14)–O(14)	1.445(4)
C(16)–C(17)	1.540(4)
C(16)–C(18)	1.497(5)
C(16)–O(12)	1.423(3)
C(16)–O(14)	1.438(4)
C(19)–O(3)	1.437(4)

The absolute configuration determination of compound (**23**) was confirmed by measuring the intensity data to include all of the Friedel reflection pairs measured successively. The reflection pairs with the most significant differences were then analysed. Reflection pairs with a calculated theoretical Bijvoet ratio >7, together with an observed intensity difference >2 standard deviations were chosen. Twenty-five such reflection pairs were

Table 7. Bond angles (°) with standard deviations in parentheses for compound (**23**).

C(2)–C(1)–C(10)	120.4(2)
C(2)–C(1)–O(1)	117.1(2)
C(10)–C(1)–O(1)	122.5(2)
C(1)–C(2)–C(3)	119.2(2)
C(2)–C(3)–C(4)	121.5(2)
C(2)–C(3)–O(3)	124.3(2)
C(4)–C(3)–O(3)	114.2(2)
C(3)–C(4)–C(5)	119.2(2)
C(4)–C(5)–C(6)	119.0(2)
C(4)–C(5)–C(10)	120.8(2)
C(6)–C(5)–C(10)	120.2(2)
C(5)–C(6)–C(7)	117.9(2)
C(5)–C(6)–O(6)	121.8(2)
C(7)–C(6)–O(6)	120.3(2)
C(6)–C(7)–C(8)	120.8(2)
C(6)–C(7)–C(11)	116.0(2)
C(8)–C(7)–C(11)	123.2(2)
C(7)–C(8)–C(9)	121.9(2)
C(7)–C(8)–C(14)	121.4(2)
C(9)–C(8)–C(14)	116.7(2)
C(8)–C(9)–C(10)	118.7(2)
C(8)–C(9)–O(9)	120.0(2)
C(10)–C(9)–O(9)	121.4(2)
C(1)–C(10)–C(5)	118.9(2)
C(1)–C(10)–C(9)	120.7(2)
C(5)–C(10)–C(9)	120.4(2)
C(7)–C(11)–C(12)	111.4(2)
C(11)–C(12)–C(13)	106.9(3)
C(11)–C(12)–C(15)	111.4(2)
C(11)–C(12)–O(12)	103.7(2)
C(13)–C(12)–C(15)	114.1(3)
C(13)–C(12)–O(12)	110.0(2)
C(15)–C(12)–O(12)	110.3(3)
C(12)–C(13)–C(14)	106.8(3)
C(8)–C(14)–C(13)	110.0(2)
C(8)–C(14)–O(14)	110.6(2)
C(13)–C(14)–O(14)	110.9(2)
C(17)–C(16)–C(18)	110.9(3)
C(17)–C(16)–O(12)	112.0(3)
C(17)–C(16)–O(14)	109.8(3)
C(18)–C(16)–O(12)	105.4(3)
C(18)–C(16)–O(14)	107.0(3)
O(12)–C(16)–O(14)	111.5(3)
C(3)–O(3)–C(19)	117.3(2)
C(12)–O(12)–C(16)	119.8(2)
C(14)–O(14)–C(16)	115.7(2)

identified and of these 21 had their differences in the same correct sense thus confirming the absolute configuration determination. A similar analysis was attempted for the weaker data of compound (**20**). Despite lowering the criteria to a Bijvoet ratio of 3, only 5 reflection pairs were identified but all of these differences were in the same correct sense.

Experimental

Mps were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded as potassium bromide discs on a Perkin-Elmer 983G spectrophotometer, UV spectra on a Varian SuperScan 3 spectrophotometer, ^1H and ^{13}C NMR spectra on a JEOL-JNM GX-400 spectrometer operating at 399.65 MHz (^1H) and 100.40 MHz (^{13}C) for solutions in deuteriochloroform, mass spectra on a V.G. Micromass 7070F instrument at 70 eV (unless stated otherwise), and optical rotations on either a Perkin-Elmer 241 MC or 141 polarimeter. All TLC and preparative TLC (PLC) was carried out on Merck Kieselgel 60 F_{254} (analytical, 0.25 mm precoated; preparative, 1 mm on glass). Column chromatography employed Mallinckrodt CC-7 and Merck Kieselgel 60 silica gel. Solutions in organic solvents were routinely dried over Na_2SO_4 prior to evaporation under reduced pressure.

Voucher specimens of *Dermocybe splendida* used in this work are deposited in the herbariums of the Royal Botanic Garden, Edinburgh, UK and the New South Wales Department of Agriculture Chemical and Biological Research Station, Rydalmere, NSW, Australia under accession numbers WAT 18086 and DAR 50092, respectively.

Isolation of Austrocortirubin (**6**), (1S,3S)-*Austrocortilutein* (**8**), and (1S,3R)-*Austrocortilutein* (**10**) *from* Dermocybe splendida.— Fresh fruit bodies were collected from mixed *Eucalyptus* forest near Marysville, Victoria during June and July, 1984–1986. A quantity (400 g) was chopped and exhaustively extracted with ethanol (6 × 500 ml) at room temperature. The combined extracts were concentrated and washed with light petroleum (b.p. 60–80 °C) to remove lipids, then distributed between water (200 ml) and ethyl acetate (3 × 200 ml). The organic phase was separated, dried, and evaporated to dryness leaving a deep red solid (1.1 g) which was dissolved in a mixture of benzene–ethyl formate–formic acid (10:5:3) and applied to a column of silica gel (15 × 4 cm) in order to separate tractable from intractable (baseline) material. Evaporation of the eluate and chromatography [PLC, benzene–ethyl formate–formic acid (50:49:1)] of the residue separated two distinct zones: (*a*) a minor, mobile zone containing the anthraquinones (**12**) and (**13**),[12] and (*b*) a major, polar zone containing the pigments (**6**), (**8**), and (**10**). Further, repeated, PLC using benzene–ethyl formate–formic acid (75:24:1) (three consecutive developments) gave in order of increasing R_F: (1S,3S)-(+)-*austrocortirubin* (**6**) (165 mg, 4.1 × 10^{-2}% of the fresh wt. of the fungus), R_F 0.32 [benzene–ethyl formate–formic acid (10:5:3)], as dark red needles, m.p. 193–195 °C from benzene–light petroleum (b.p. 60–80 °C) (Found: C, 60.0; H, 4.8. $C_{16}H_{16}O_7$ requires C, 60.0; H, 5.0%); $[\alpha]_D^{20}$ + 34° (*c* 0.543 in $CHCl_3$); ν_{max} 1 601 cm^{-1}; λ_{max}(EtOH) 226 (log ε 4.51), 302 (3.96), 475 (3.85), 504 (3.91), and 541 nm (3.71); δ_H see Table 1; δ_C 30.4 (q, *J* 126.1 Hz, 3-Me), 37.7 and 40.1 (each br t, *J* 128.4 Hz, C-2 and C-4), 56.9 (q, *J* 146.7 Hz, 6-OMe), 62.7 (dd, *J* 149.7 and 4.4 Hz, C-1), 68.1 (m, C-3), 108.0 (t, *J* 4.4 Hz, C-8a), 109.6 (d, *J* 164.3 Hz, C-7), 110.1 (d, *J* 4.4 Hz, C-10a), 136.0 and 138.2 (each m, C-4a and C-9a), 158.5 and 160.5 (each m, C-9 and C-10), 160.2 (pent., *J* 4.4 Hz, C-6), 178.3 (d, *J* 7.4 Hz, C-5), and 184.4 (s, C-8); *m/z* (15 eV) 320 (M^+, 60%), 304 (12), 303 (17), 302 (100), 300 (18), 287 (24), 285 (18), 284 (89), 260 (37), 259 (36), 245 (30), 244 (54), and 242 (14); (1S,3R)-(+)-*austrocortilutein* (**10**) (6 mg, 1.5 × 10^{-3}% of the fresh wt. of the fungus), R_F 0.34 [benzene–ethyl formate–formic acid (10:5:3)], as orange-yellow needles, m.p. 162–164 °C from chloroform–light petroleum (b.p. 60–80 °C) (Found: C, 62.8; H, 5.1. $C_{16}H_{16}O_6$ requires C, 63.15; H, 5.3%); $[\alpha]_D^{20}$ + 288° (*c* 0.100 in $CHCl_3$); ν_{max} 1 665, 1 631, and 1 596 cm^{-1}; λ_{max}(EtOH) 219 (log ε 4.44), 269 (4.18), 284sh (3.95), and 430 nm (3.65); δ_H: see Table 1; *m/z* (15 eV) 304 (M^+, 12%), 288 (20), 287 (17), 286 (100), 284 (41), 271 (13), 269 (17), and 268 (95); and (1S,3S)-(+)- *austrocortilutein* (**8**) (89 mg, 2.2 × 10^{-2}% of the fresh wt. of the fungus), R_F 0.36 [benzene–ethyl formate–formic acid (10:5:3)], as orange-yellow needles, m.p. 183–185 °C from chloroform–light petroleum (b.p. 60–80 °C) (Found: C, 62.8; H, 5.05. $C_{16}H_{16}O_6$ requires C, 63.15; H, 5.3%); $[\alpha]_D^{20}$ + 52° (*c* 0.095 in $CHCl_3$); ν_{max} 1 667, 1 639, 1 605, and 1 574 cm^{-1}; λ_{max} (EtOH) 221 (log ε 4.56), 269 (4.19), 283sh (3.98), and 428 nm (3.63); δ_H: see Table 1; δ_C 29.9 (q, *J* 126.2 Hz, 3-Me), 37.6 and 39.8 (each br t, *J* 128.4 and 126.2 Hz, respectively, C-2 and C-4), 55.8 (q, *J* 145.3 Hz, 6-OMe), 62.1 (dd, *J* 149.7 and 4.4 Hz, C-1), 67.9 (m, C-3), 105.6 (ddd, *J* 161.4, 7.4, and 4.4 Hz, C-7), 107.5 (dd, *J* 167.2 and 5.9 Hz, C-5), 108.7 (q, *J* 5.9 Hz, C-8a), 132.8 (s, C-10a), 141.2 and 142.5 (each m, C-4a and C-9a), 163.5 (t, *J* 4.4 Hz, C-8), 165.2 (m, C-6), 183.5 (s, C-10),

and 187.1 (s, C-9); *m/z* (15 eV) 304 (M^+, 100%), 287 (23), 286 (100), 271 (10), 268 (12), 262 (36), 247 (16), 246 (78), 245 (11), 244 (67), and 243 (18).

Treatment of Quinones (**6**), (**8**), *and* (**10**) *with Acetic Anhydride.*—A solution of austrocortirubin (10 mg, 0.031 mmol) in acetic anhydride (4 ml) containing concentrated sulphuric acid (1 drop) was warmed at 40 °C for 3 h. The solution was cooled, diluted with ice–water (15 ml) and the product isolated with ethyl acetate. Evaporation of the (dried) organic phase gave austrocortinin diacetate (**14**) (10 mg, 87%) as canary yellow needles, m.p. 241–246 °C (lit.,[12] 245–252 °C; lit.,[15] 242–248 °C) from chloroform–light petroleum (b.p. 60–80 °C), identical with an authentic sample.

Similar treatment of (1*S*,3*S*)-austrocortilutein and of (1*S*,3*R*)-austrocortilutein gave 1-acetoxy-3-methoxy-6-methyl-9,10-anthraquinone (**15**) as pale yellow needles, m.p. 171–173 °C (lit.,[12] 173–177 °C; lit.,[18] 171–173 °C) from chloroform–light petroleum (b.p. 60–80 °C), identical with an authentic sample.

Acetonide Derivatives.—Austrocortirubin (20 mg, 0.062 mmol) in dichloromethane (3 ml) containing 2,2-dimethoxypropane (2 ml) and *p*-toluenesulphonic acid (5 mg) was stirred at 30 °C over 16 h. The mixture was diluted with chloroform (15 ml) and washed successively with aqueous sodium hydrogen carbonate (10 ml; 2M) and buffer (10 ml, pH 7.4). Evaporation of the (dried) organic phase and purification of the residue by preparative TLC with benzene–ethyl formate–formic acid (50:49:1) as eluant gave (1S,3S)-(+)-*austrocortirubin acetonide* (**19**) (19 mg, 83%) as crimson needles, m.p. 264–268 °C from chloroform–light petroleum (b.p. 60–80 °C) (Found: C, 62.85; H, 5.3. $C_{19}H_{20}O_7$ requires C, 63.3; H, 5.6%); $[\alpha]_D^{20}$ + 189° (*c* 0.308 in $CHCl_3$); ν_{max} 1 597 cm^{-1}; λ_{max}(EtOH) 226 (log ε 4.45), 301 (3.89), 476sh (3.82), 504 (3.87), and 540 nm (3.68); δ_H 1.11 (3 H, s, 3-Me), 1.53 and 1.54 (each 3 H, s, CMe_2), 1.69 (1 H, dd, *J* 13.9 and 2.9 Hz, 2-H_a), 2.52 (1 H, d, *J* 18.7 Hz, 4-H_a), 2.62 (1 H, ddd, *J* 13.9, 2.9, and 1.8 Hz, 2-H_e), 3.12 (1 H, dd, *J* 18.7 and 1.8 Hz, 4-H_e), 3.94 (3 H, s, 6-OMe), 5.39 (1 H, t, *J* 2.9 Hz, 1-H), 6.20 (1 H, s, 7-H), and 12.64 and 13.24 (each 1 H, s, *peri*-OH); *m/z* 360 (M^+, 7%), 302 (22), 287 (11), 286 (19), 285 (100), 284 (23), 43 (38), and 18 (18).

Similarly prepared from (1*S*,3*S*)-austrocortilutein (22 mg, 0.072 mmol) was (1S,3S)-(+)-*austrocortilutein acetonide* (**23**) (20 mg, 80%) as yellow needles, m.p. 192–195 °C from chloroform–light petroleum (b.p. 60–80 °C) (Found: C, 66.4; H, 6.05. $C_{19}H_{20}O_6$ requires C, 66.3; H, 5.85%); $[\alpha]_D^{20}$ + 60° (*c* 0.297 in $CHCl_3$); ν_{max} 1 663, 1 633, and 1 599 cm^{-1}; λ_{max}(EtOH) 220 (log ε 4.52), 268 (4.16), 283sh (3.89), and 428 nm (3.63); δ_H 1.20 (3 H, s, 3-Me), 1.51 and 1.53 (each 3 H, s, CMe_2), 1.59 (1 H, dd, *J* 13.9 and 2.9 Hz, 2-H_a), 2.35 (1 H, d, *J* 19.8 Hz, 4-H_a), 2.61 (1 H, ddd, *J* 13.9, 2.9, and 1.8 Hz, 2-H_e), 2.93 (1 H, dd, *J* 19.8 and 1.8 Hz, 4-H_e), 3.90 (3 H, s, 6-OMe), 5.28 (1 H, t, *J* 2.9 Hz, 1-H), 6.66 (1 H, d, *J* 2.6 Hz, 7-H), 7.18 (1 H, d, *J* 2.6 Hz, 5-H), and 12.38 (1 H, s, *peri*-OH); *m/z* (15 eV) 344 (M^+, 1%), 330 (52), 329 (100), 286 (10), 271 (17), 270 (99), 269 (100), 268 (17), and 244 (19).

Arylboronate Derivatives.—Austrocortirubin (28 mg, 0.087 mmol), phenylboronic acid (12 mg, 0.098 mmol), and *p*-toluenesulphonic acid (7 mg) were stirred together in dichloromethane (5 ml) at room temperature for 18 h. The mixture was diluted with chloroform (10 ml) and washed successively with aqueous sodium hydrogen carbonate (10 ml; 2M) and buffer (10 ml; pH 7.4). Evaporation of the (dried) organic phase and purification of the residue by preparative TLC with benzene–ethyl formate–formic acid (50:49:1) as eluant gave (1S,3S)-(+)-*austrocortirubin phenylboronate* (**20**) (30 mg, 83%) as crimson needles, m.p. 225–226 °C from chloroform–light petroleum (b.p. 60–80 °C) (Found: C, 65.2; H, 4.7. $C_{22}H_{19}BO_7$ requires C, 65.1; H, 4.7%); $[\alpha]_D^{20}$ + 277° (*c* 0.300 in $CHCl_3$); ν_{max} 1 600 cm^{-1}; λ_{max}(EtOH) 226 (log ε 4.54), 303 (3.94), 477sh (3.82), 505 (3.89), and 542 nm (3.69); δ_H 1.65 (3 H, s, 3-Me), 2.04 (1 H, dd, *J* 13.9 and 2.2 Hz, 2-H_a), 2.32 (1 H, ddd, *J* 13.9, 2.9, and 1.8 Hz, 2-H_e), 2.78 (1 H, d, *J* 19.4 Hz, 4-H_a), 3.32 (1 H, dd, *J* 19.4 and 1.8 Hz, 4-H_e), 3.93 (3 H, s, 6-OMe), 5.71 (1 H, dd, *J* 2.9 and 2.2 Hz, 1-H), 6.19 (1 H, s, 7-H), 7.29 (2 H, ddm, *J* 8.1 and 7.3 Hz, Ar-H_2), 7.37 (1 H, tm, *J* 7.3 Hz, Ar-H), 7.77 (2 H, dm, *J* 8.1 Hz, Ar-H_2), and 12.60 and 13.25 (each 1 H, s, *peri*- OH); *m/z* 406 (M^+, 100%), 405 (24), 363 (10), 362 (10), 349 (50), 348 (17), 347 (17), 284 (14), 260 (11), 259 (23), 105 (20), 77 (10), 69 (13), 43 (45), 31 (22), and 18 (87).

Similarly prepared from austrocortirubin (22 mg, 0.069 mmol) using *p*-bromophenylboronic acid (15 mg, 0.075 mmol) was (1S,3S)-(+)-*austrocortirubin* p-*bromophenylboronate* (**21**) (28 mg, 85%) as crimson needles, m.p. 228–229 °C from chloroform–light petroleum (b.p. 60–80 °C) (Found: C, 54.7; H, 4.0. $C_{22}H_{18}BBrO_7$ requires C, 54.5; H, 3.7%); $[\alpha]_D^{20}$ + 218° (*c* 0.299 in $CHCl_3$); ν_{max} 1 599 and 1 587 cm^{-1}; λ_{max}(EtOH) 227 (log ε 4.62), 303 (3.95), 476sh (3.84), 505 (3.90), and 541 nm (3.71); δ_H 1.64 (3 H, s, 3-Me), 2.04 (1 H, dd, *J* 13.9 and 2.2 Hz, 2-H_a), 2.31 (1 H, ddd, *J* 13.9, 2.9, and 1.8 Hz, 2-H_e), 2.79 (1 H, d, *J* 19.4 Hz, 4-H_a), 3.30 (1 H, dd, *J* 19.4 and 1.8 Hz, 4-H_e), 3.93 (3 H, s, 6-OMe), 5.70 (1 H, dd, *J* 2.9 and 2.2 Hz, 1-H), 6.19 (1 H, s, 7-H), 7.42 and 7.61 (each 2 H, dm, *J* 8.4 Hz, Ar-H), and 12.59 and 13.25 (each 1 H, s, *peri*-OH); *m/z* 487 (M^+ + 3, 22%), 486 (M^+ + 2, 96), 485 (M^+ + 1, 44), 484 (M^+, 100), 483 (25), 442 (10), 429 (38), 428 (19), 427 (46), 426 (13), 425 (17), 285 (17), 284 (23), 269 (11), 260 (19), 259 (44), 243 (11), 242 (13), 77 (15), 69 (11), 43 (48), and 36 (10).

(1*S*,3*S*)-Austrocortilutein (28 mg, 0.092 mmol) with phenylboronic acid (13 mg, 0.017 mmol) gave (1S,3S)-(+)-*austrocortilutein phenylboronate* (**24**) (31 mg, 86%) as yellow needles, m.p. 179–181 °C from chloroform–light petroleum (b.p. 60–80 °C) (Found: C, 67.3; H, 5.1. $C_{22}H_{19}BO_6$ requires C, 67.7; H, 4.9%); $[\alpha]_D^{20}$ + 71° (*c* 0.300 in $CHCl_3$); ν_{max} 1 659, 1 637, 1 614, and 1 600 cm^{-1}; λ_{max}(EtOH) 220 (log ε 4.60), 269 (4.21), 284sh (3.96), and 427 nm (3.66); δ_H 1.62 (3 H, s, 3-Me), 1.96 (1 H, dd, *J* 13.9 and 2.2 Hz, 2-H_a), 2.28 (1 H, ddd, *J* 13.9, 2.9, and 1.8 Hz, 2-H_e), 2.65 (1 H, d, *J* 20.2 Hz, 4-H_a), 3.14 (1 H, dd, *J* 20.2 and 1.8 Hz, 4-H_e), 3.89 (3 H, s, 6-OMe), 5.58 (1 H, dd, *J* 2.9 and 2.2 Hz, 1-H), 6.65 (1 H, d, *J* 2.6 Hz, 7-H), 7.16 (1 H, d, *J* 2.6 Hz, 5-H), 7.30 (2 H, ddm, *J* 8.1 and 7.3 Hz, Ar-H_2), 7.39 (1 H, tm, *J* 7.3 Hz, ArH), 7.77 (2 H, dm, *J* 8.1 Hz, Ar-H_2), and 12.31 (1 H, s, *peri*-OH); *m/z* 390 (M^+, 78%), 389 (19), 348 (45), 347 (22), 334 (21), 333 (100), 332 (24), 286 (21), 269 (12), 268 (44), 244 (15), 243 (28), 151 (12), 122 (12), 105 (18), 78 (33), 77 (14), 51 (15), 43 (45), and 18 (19), and with *p*-bromophenylboronic acid gave (1S,3S)-(+)-*austrocortilutein* p-*bromophenylboronate* (**25**) (79%) as yellow needles, m.p. 196–198 °C from chloroform–light petroleum (b.p. 60–80 °C) (Found: C, 56.7; H, 4.0. $C_{22}H_{18}BBrO_6$ requires C, 56.3; H, 3.9%); $[\alpha]_D^{20}$ + 23° (*c* 0.400 in $CHCl_3$); ν_{max} 1 660, 1 637, 1 614, and 1 585 cm^{-1}; λ_{max}(EtOH) 220 (log ε 4.63), 231sh (4.34), 268 (4.17), 283sh (3.92), and 427 nm (3.61); δ_H 1.61 (3 H, s, 3-Me), 1.96 (1 H, dd, *J* 13.9 and 2.6 Hz, 2-H_a), 2.27 (1 H, ddd, *J* 13.9, 2.9, and 1.8 Hz, 2-H_e), 2.65 (1 H, d, *J* 20.2 Hz, 4-H_a), 3.13 (1 H, dd, *J* 20.2 and 1.8 Hz, 4-H_e), 3.89 (3 H, s, 6-OMe), 5.57 (1 H, dd, *J* 2.9 and 2.6 Hz, 1-H), 6.65 (1 H, d, *J* 2.6 Hz, 7-H), 7.16 (1 H, d, *J* 2.6 Hz, 5-H), 7.43 and 7.62 (each 2 H, dm, *J* 8.4 Hz, Ar-H), and 12.29 (1 H, s, *peri*-OH); *m/z* 471 (M^+ + 3, 24%), 470 (M^+ + 2, 100), 469 (M^+ + 1, 46), 468 (M^+, 100), 467 (22), 429 (11), 428 (56), 427 (35), 426 (60), 425 (26), 414 (20), 413 (99), 412 (43), 411 (97), 410 (24), 286 (51), 271 (13), 269 (21), 268 (57), 244 (28), 243 (53), 151 (20), 115 (15), 103 (12), 85 (17), 83 (30), 77 (23), 76 (10), 51 (15), 43 (61), and 18 (16).

Oxidative Degradation.—Austrocortirubin (46 mg, 0.144

mmol) in methanol (20 ml) was exposed to hydrogen essentially as described previously.[13] Purification of the products by preparative TLC with benzene–ethyl formate–formic acid (50:49:1) as eluant gave (3*R*)-1-deoxyaustrocortirubin (**7**) (30 mg, 82%), m.p. 211–216 °C, $[\alpha]_D^{20}$ − 59° (*c* 0.049 in $CHCl_3$) and (3*R*)-1-deoxyaustrocortilutein (**9**) (2 mg, 5%), m.p. 206–212 °C, $[\alpha]_D^{20}$ − 77° (*c* 0.061 in $CHCl_3$), both identical with authentic materials.[13]

To (−)-1-deoxyaustrocortirubin (63 mg, 0.207 mmol) in a heterogeneous mixture of carbon tetrachloride (6 ml), acetonitrile (6 ml), and water (9 ml) containing sodium metaperiodate (1.328 g, 30 equiv.) was added a trace of ruthenium(III) trichloride trihydrate and the mixture was stirred vigorously at room temperature during 24 h. Propan-2-ol (1 ml) was added followed by barium chloride (1 g) and the mixture was stirred vigorously for a further 30 min. The suspension was filtered and the residue washed with dichloromethane (10 ml). The filtrate was extracted with further portions of dichloromethane (3 × 10 ml). The aqueous phase remaining was acidified to Congo Red with dilute hydrochloric acid and continuously extracted with ether during 18 h. The (dried) dichloromethane and ether extracts were combined and evaporated to dryness to afford the carboxylic acid (**26**) which was not purified further. The carboxylic acid (**26**) was treated dropwise with ethereal diazomethane until evolution of nitrogen ceased. The solvent was removed under reduced pressure and the residue was chromatographed on a flash column eluted with ether–light petroleum (b.p. 60–80 °C) (9:1) to afford (2*R*)-methyl 2-(2′-methyl-5′-oxotetrahydrofuryl)acetate (**27**) (16 mg, 45%) as a colourless oil, b.p. 65–75 °C at 0.05 mmHg (Kugelrohr), $[\alpha]_D^{20}$ + 9.8° (*c* 2.19 in $CHCl_3$), identical in all respects with an authentic sample.[20]

In an entirely analogous sequence of reactions (1*S*,3*S*)-austrocortilutein (**8**) was converted first to (3*R*)-1-deoxyaustrocortilutein (**9**) (90%), m.p. 206–212 °C, $[\alpha]_D^{20}$ − 78° (*c* 0.051 in $CHCl_3$) then to ester (**27**) (40%), $[\alpha]_D^{20}$ + 9.8° (*c* 2.05 in $CHCl_3$).

Hydrogenolysis of (1S,3R)-*Austrocortilutein*.—(1*S*,3*R*)-austrocortilutein (12 mg, 0.039 mmol) in methanol (5 ml) was exposed to hydrogen in the presence of palladium on charcoal (23 mg; 10%) until consumption was complete (*ca.* 1 h). The catalyst was filtered off and washed with methanol and the filtrate evaporated under reduced pressure. Purification of the residue using preparative TLC with benzene–ethyl formate–formic acid (50:49:1) gave (3*S*)-1-deoxyaustrocortilutein (**11**) (10 mg, 88%) as orange plates, m.p. 206–211 °C from chloroform–light petroleum (b.p. 60–80 °C), $[\alpha]_D^{20}$ + 73° (*c* 0.060 in $CHCl_3$), identical in all other respects (IR, UV, ^1H NMR and mass spectroscopy), with its antipode (**9**).[13]

Acknowledgements

We thank Dr R. Watling, Royal Botanic Garden, Edinburgh, and Dr J. Walker, New South Wales Department of Agriculture Chemical and Biological Research Station, Rydalmere, NSW, for help in identifying fungi and for lodging herbarium specimens; Dr E. Horak, E. T. H., Zurich, for comparison of our collection with *Dermocybe splendida* type; and Messrs T. May and B. A. Fuhrer, Monash University, for continuing help with taxonomy and nomenclature. Professor T. Anke, University of Kaiserslautern kindly performed the antimicrobial assays. We are grateful to Professor T. R. Kelly for a synthetic sample of austrocortinin (**12**) and to Dr A. Stoessl for samples of the natural product (**13**) and its acetate (**15**). The Australian Research Grants Scheme provided financial support; A.F.S. is the recipient of a Commonwealth Postgraduate Research Award.

References

1 Part 11; M. Gill and A. Gimenez, *J. Chem. Soc., Perkin Trans. 1*, in the press.
2 Preliminary communication: M. Gill and R. J. Strauch, *Tetrahedron Lett.*, 1985, **26**, 2593.
3 A. Stoessl, *J. Chem. Soc., Chem. Commun.*, 1967, 307; *Can. J. Chem.*, 1969, **47**, 767, 777.
4 A. M. Becker, R. W. Rickards, K. J. Schmalzl, and H. C. Yick, *J. Antibiot.*, 1978, **31**, 324.
5 T. Noda, T. Take, M. Otani, K. Miyauchi, T. Watanabe, and J. Abe, *Tetrahedron Lett.*, 1968, 6087; A. Takenaka, A. Furusaki, T. Watanabe, T. Noda, T. Take, T. Watanabe, and J. Abe, *Tetrahedron Lett.*, 1968, 6091; T. Noda, T. Take, T. Watanabe, and J. Abe, *Tetrahedron*, 1970, **26**, 1339.
6 R. Charudattan and K. V. Rao, *Appl. Env. Microbiol.*, 1982, **43**, 846.
7 B. A. Fuhrer, 'A Field Companion to Australian Fungi,' Five Mile Press, Melbourne, 1985, p. 13.
8 E. Horak, *Aust. J. Bot. Suppl. Ser.*, 1983, **10**, 1.
9 G. Keller, Ph.D. Thesis, University of Innsbruck, 1979; E. Horak, *Sydowia*, 1987, **40**, 81; G. Keller, M. Moser, E. Horak, and W. Steglich, *Sydowia*, 1987, **40**, 169.
10 M. Gill and W. Steglich, *Fortschr. Chem. Org. Naturst.*, 1987, **51**, 125.
11 M. Moser, *Schweiz. Z. Pilzkd.*, 1972, **50**, 151.
12 M. A. Archard, M. Gill, and R. J. Strauch, *Phytochemistry*, 1985, **24**, 2755.
13 M. Gill and A. F. Smrdel, *Phytochemistry*, 1987, **26**, 2999.
14 R. H. Thomson, 'Naturally Occurring Quinones,' 2nd edn., Academic Press, London, 1971; 3rd edn., Chapman-Hall, London, 1987.
15 T. R. Kelly, *Tetrahedron Lett.*, 1978, 1387.
16 T. R. Kelly, J. K. Saha, and R. R. Whittle, *J. Org. Chem.*, 1985, **50**, 3679.
17 R. E. Moore and P. J. Scheuer, *J. Org. Chem.*, 1966, **31**, 3272.
18 A. Stoessl, *Can. J. Chem.*, 1969, **47**, 777.
19 P. H. J. Carlsen, T. Katsuki, V. S. Martin, and K. B. Sharpless, *J. Org. Chem.*, 1981, **46**, 3936.
20 M. Gill and A. F. Smrdel, submitted for publication in *Tetrahedron*.
21 O. Toshikazu, Y. Marsuzawa, K. Koyoshima, A. Yoshimoto, H. Naganawa, T. Takeuchi, and H. Umezawa, *J. Antibiot.*, 1981, **34**, 783.
22 T. Anke, University of Kaiserslautern, personal communication.
23 C. B. M. Kidd, B. Caddy, J. Robertson, I. R. Tebbett, and R. Watling, *Trans. Brit. Mycol. Soc.*, 1985, **85**, 213; I. Gruber, *Z. Pilzkd*, 1970, **36**, 95; G. Keller, *Sydowia*, 1982, **35**, 110; G. Keller and J. F. Ammirati, *Mycotaxon*, 1983, **18**, 357; K. Hoiland, *Opera Bot.*, 1983, **71**, 1; M. Gill and W. Steglich, ref. 10.
24 M. Gill, A. Gimenez, A. G. Jhingran, and A. F. Smrdel, *Phytochemistry*, 1989, **28**, 2647.
25 J. R. Carruthers, 'CRYSTALS User Manual,' Oxford University Computing Laboratory, 1975.
26 P. Mains, S. L. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, 'MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data,' Universities of York, England and Louvain, Belgium, 1980.
27 M. J. Begley, *Acta Crystallogr., Sect. A*, 1987, **43**, C-284.
28 W. C. Hamilton, *Acta Crystallogr.*, 1965, **18**, 502; D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.

Paper 9/03997J
Received 19*th September* 1989
Accepted 4*th January* 1990