Metabolites of *Aspergillus ustus*. Part 2.[1] Stereoelectronic Control in the Acid-catalysed Hydrolysis of the Ortho Ester Moiety in Austalides A—F

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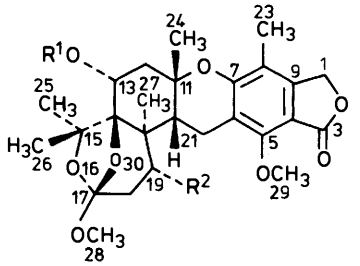
Attempted acetylation of the C-13 hydroxy function in austalides B (**2**) and D (**4**) with either acetic anhydride and pyridine or 4-dimethylaminopyridine fails. Acetylation occurs under more forcing conditions using acetic anhydride and catalytic amounts of perchloric acid, but the major products are in each case δ-lactone derivatives. It is shown that the formation of a δ- instead of an ε-lactone from the ortho ester moiety is favoured because initial cleavage of the C(17)–O(16) bond is stereoelectronically assisted by the two other oxygen atoms, O-30 and O-35, since each has a lone-pair orbital antiperiplanar to this bond.

The structure elucidation of the austalides A—F [(**1**)—(**6**)], novel meroterpenoid metabolites isolated from cultures of *Aspergillus ustus* (Bainier) Thom. and Church (strain MRC 1163), as outlined in the preceding paper[1] is based mainly on data obtained from high-field ^1H and ^{13}C n.m.r. spectra. The close structural relationship between these metabolites was confirmed chemically by mild alkaline hydrolysis (0.1M-potassium hydroxide in methanol) of austalide A (**1**) to give austalide B (**2**) and of austalides C (**3**), D (**4**), and E (**5**) to give, in each case, austalide F (**6**). Acetylation of the C-19 hydroxy group in austalide E (**5**) with acetic anhydride in pyridine proceeded smoothly to give austalide C (**3**). In contrast, attempted acetylation of the C-13 hydroxy group in austalide D (**4**) and B (**2**) with acetic anhydride and either pyridine or 4-dimethylaminopyridine failed and only starting material was recovered.[1]

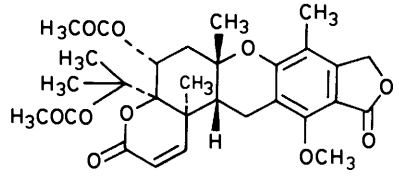
The C-13 hydroxy group in austalide D (**4**) was acetylated under more forcing conditions with acetic anhydride and catalytic amounts of perchloric acid at −78 °C. The mixture was allowed to attain room temperature and the reaction quenched by the addition of a sodium hydrogen carbonate–ice mixture. Austalide C (**3**) was obtained as a minor product in addition to the two δ-lactones (**7**) ($C_{29}H_{34}O_{10}$, M^+ 542) and (**8**) ($C_{31}H_{38}O_{12}$, M^+ 602). The ^1H n.m.r. spectrum of the δ-lactone (**8**) indicated the presence of three isolated ABX spin systems which are ascribed to the C-12 and C-13 protons [δ_H 2.286, *J* 16.2 and 4.1 Hz, 12-H_b; δ_H 2.516 *J* 16.2 and 2.3 Hz, 12-H_a; δ_H 5.305, *J* 4.1 and 2.3 Hz, 13-H], the C-18 and C-19 protons [δ_H 2.718, *J* 20.0 Hz, 18-H_b; δ_H 3.097, *J* 20.0 and 8.5 Hz, 18-H_a; δ_H 5.594, *J* 8.5 Hz, 19-H], and the C-21 and C-22 protons [δ_H 2.969, *J* 18.9 and 8.3 Hz, 22-H_b; δ_H 3.200, *J* 18.9 Hz, 22-H_a; δ_H 1.913, *J* 8.3 Hz, 21-H]. The assignment of these resonances is based on chemical-shift considerations, the magnitude of the geminal and vicinal (H,H) coupling constants, and the results obtained from ^1H-{^1H} decoupling experiments. The magnitude (*J* 20.0 Hz) of the geminal coupling constant of the C-18 protons reflects their location adjacent to the C-17 carbonyl group.[2]

The signals of the carbonyl carbon atoms of six- and seven-membered lactones appear at approximately δ_C 167 and δ_C 176, respectively.[3] The presence of a six-membered lactone moiety in (**8**) is, therefore, confirmed by the chemical-shift value of the C-17 carbonyl group (δ_C 167.76) in the broad-band proton-decoupled ^{13}C n.m.r. spectrum.

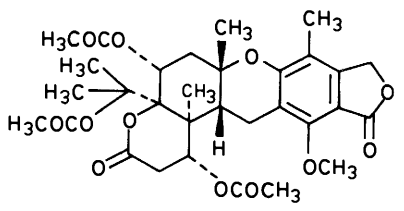
A comparison of the ^1H n.m.r. spectra of the α,β-unsaturated lactone (**7**) and the lactone (**8**) indicated that the ABX spin system due to the C-18 and C-19 protons is absent in the spectrum of (**7**). Instead, the olefinic protons, 18-H and 19-H, give rise to an AX spin system (δ_H 5.959 and 6.904). The



(**1**) A: R^1 = $COCH_3$ (33 34), R^2 = H
(**2**) B: R^1 = H, R^2 = H
(**3**) C: R^1 = $COCH_3$, R^2 = $OCOCH_3$ (31 32)
(**4**) D: R^1 = H, R^2 = $OCOCH_3$
(**5**) E: R^1 = $COCH_3$, R^2 = OH
(**6**) F: R^1 = H, R^2 = OH



(**7**)



(**8**)

magnitude of the vicinal proton–proton coupling constant (*J* 9.8 Hz) is in agreement with the *Z* configuration of the double bond. The ^{13}C signals at δ_C 158.69 and δ_C 118.72 in the spectrum of (**7**) were assigned to the sp^2 carbon atoms, C-18 and C-19, respectively. The C-17 carbonyl carbon atom resonates at δ_C 161.79 which is in good agreement with the corresponding chemical shifts in α,β-unsaturated δ-lactones.[4]

Acetylation of the C-13 hydroxy group in austalide B (**2**) with acetic anhydride and perchloric acid gave austalide A as a

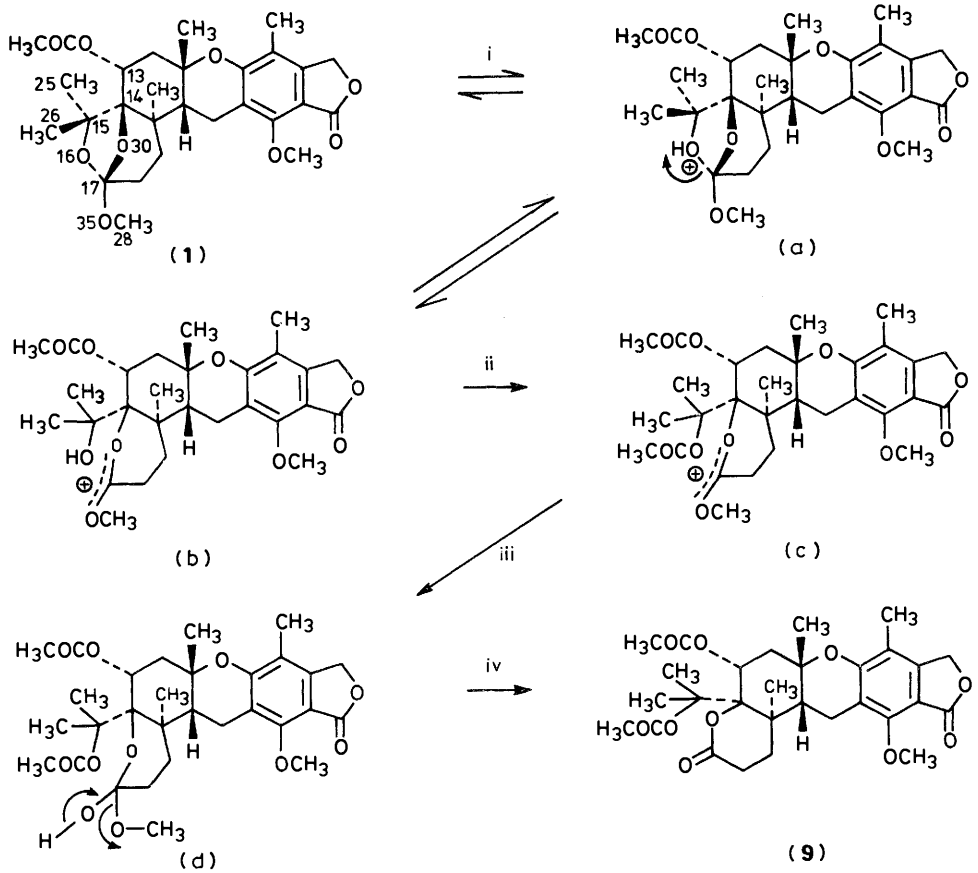


Figure 1. Proposed mechanism for the acid-catalysed cleavage of the ortho ester (**1**). (i) H^+ (ii) Ac_2O (iii) H_2O (iv) $-CH_3OH$

minor product (8%) and the bulk of the material was transformed into the δ-lactone (**9**) as indicated by the chemical-shift value of the C-17 carbonyl carbon atom (δ_C 167.79).[3] Catalytic hydrogenation of (**7**) over Pd-C (10%) yielded the δ-lactone (**9**). These results provide a chemical correlation between the structures of austalides A (**1**) and B (**2**) and those of the C-19 oxygenated austalides C—F [(**3**)—(**6**)].

The isolation of the above δ-lactones from the reaction mixtures illustrates the ease by which the ortho ester is hydrolysed by acid in the presence of acetic anhydride. The facile acid-catalysed hydrolysis of ortho esters is well known.[5] However, only starting material was obtained when austalide D (**4**) was treated with aqueous perchloric acid (40%) in dioxane or in acetic acid, or with 0.5M-hydrochloric acid in tetrahydrofuran. It would thus appear that the observed hydrolysis of the ortho ester proceeds only in the presence of acetic anhydride.

The proposed mechanism for the formation of the δ-lactones by acid-catalysed cleavage of the ortho ester moieties is shown for austalide A (**1**) in Figure 1. Reversible protonation of O-16 and cleavage of the C(17)–O(16) bond leads to the resonance-stabilized carbonium ion (b). The next step, acetylation of the tertiary hydroxy group, is irreversible and explains the prerequisite role of acetic anhydride in the reaction. Recyclisation of the dialkoxy carbonium ion (b) to give the protonated starting material must be an extremely facile process (see later) and it is only by trapping the nucleofugal oxygen (O-16) as its *O*-acetyl derivative that this process is prevented. A possible driving force for this recyclisation is the steric crowding of the C-25 and C-26 methyl groups with the C-13 acetoxy group in the dialkoxy carbonium ion (b). Hydrolysis of the carbonium ion (c) during work-up leads to the formation of the hemi-ortho ester (d)[6] which is transformed into the six-membered lactone (**9**) under the reaction conditions.

The nature of the carbonium ion (b), produced by the protonation and cleavage of the ortho ester, deserves further comment. Initial protonation of O-30 and cleavage of the C(17)–O(30) bond, or protonation of O-35 and cleavage of the C(17)–O(35) bond would lead to the carbonium ions depicted in Figures 2 and 3, respectively. However, these pathways do not offer alternatives to the proposed pathway outlined in Figure 1, because neither of the two intermediate carbonium ions leads to the product (**9**) under the conditions of the reaction.

The products of the reaction pathways shown in Figure 2 [(**10**) and (**11**)] and in Figure 3, (**12**) were never obtained, and therefore serious doubts about their validity must be entertained. This apparent lack of nucleofugal ability of O-30 and O-35, as opposed to the ease of C(17)–O(16) bond fission, can be explained on stereoelectronic grounds.

Deslongchamps postulated that reaction at tetrahedral carbon atoms bearing three heteroatoms proceeds where possible with stereoelectronic assistance.[7] Cleavage of an ortho ester carbon–oxygen bond is stereoelectronically assisted if the two other oxygen atoms each has a lone-pair orbital orientated antiperiplanar to it. In order to apply these criteria to the present work, it is necessary to consider the theoretically possible gauche conformations (i), (ii), and (iii) (Figure 4) of the ortho ester moiety in austalide A (**1**).

Conformer (i) in Figure 4 corresponds to the solid-state conformation as determined by *X*-ray crystallography of austalide A (**1**)[8] and will be considered first. This conformation is possibly also preferred in solution, since an n.O.e. was

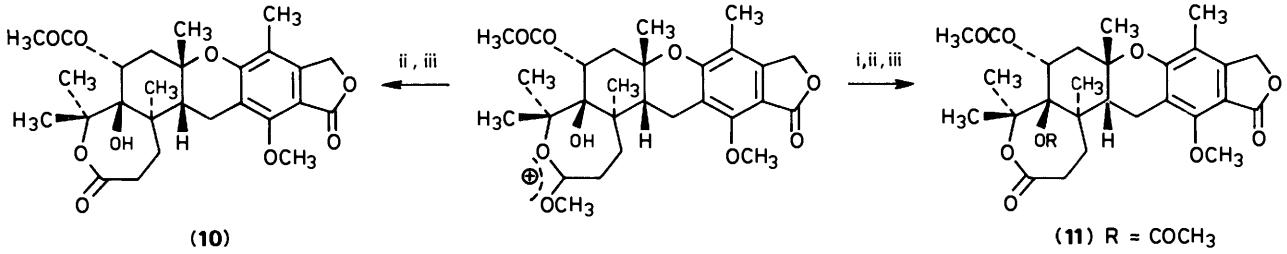


Figure 2. Hydrolysis of austalide A (**1**) *via* initial protonation of O-30. (i) Ac_2O (ii) H_2O (iii) $-CH_3OH$

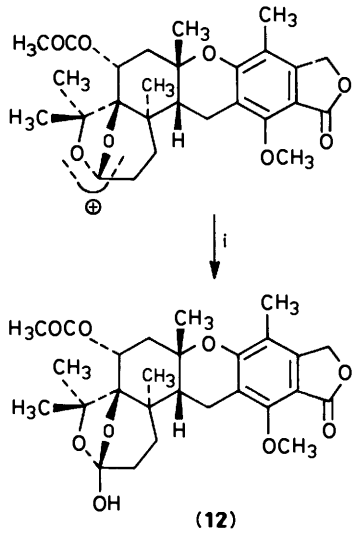


Figure 3. Hydrolysis of austalide A (**1**) *via* initial protonation of O-35. (i) H_2O

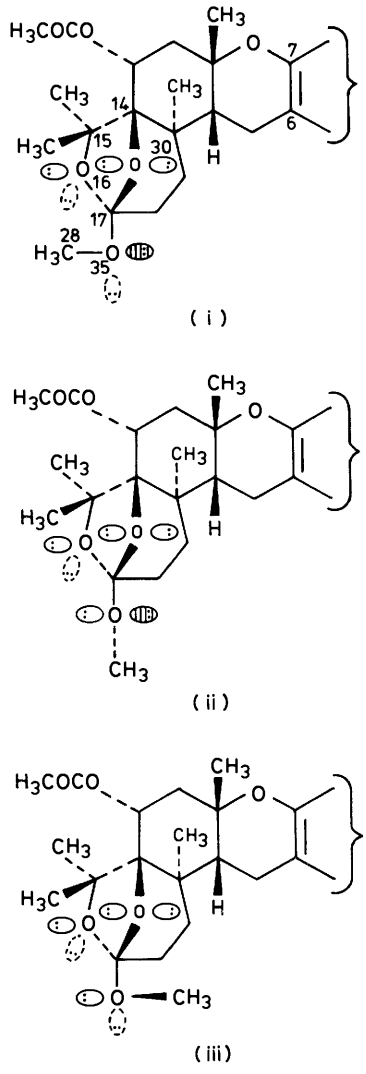


Figure 4. Gauche conformations of the ortho ester moiety in austalide A (**1**) due to free rotation of the C-17 *O*-methyl group

observed between the C-26 and C-28 methyl protons of austalide A.[1] The relevant carbon–oxygen–carbon–oxygen torsion angles obtained from the *X*-ray study (see Table) allowed the calculation of the torsion angles between an ortho ester oxygen atom and the lone-pair orbitals of each of the other two oxygen atoms [Figure 5 (a), (b), and (c)]. For this purpose it can be assumed that the oxygen atoms are sp^3 hybridized with bond angles of 120°. The small errors introduced in the calculations by this assumption do not affect the conclusions.

The calculated torsion angles between O-16 and a lone-pair orbital of each of O-30 and O-35 are 201.0° and 185.2° [Figure 5 (a) and (c), respectively]. These values are well inside the range defined as antiperiplanar (180 ± 30°), and the cleavage of the C(17)–O(16) bond is, therefore, stereoelectronically assisted. On the other hand, the calculated torsion angles between O-30 and the lone-pair orbitals of each of O-16 [Figure 5 (b)] and O-35 [Figure 5 (c)] are 133.2° and 253.2°, and 183.7° and 303.7°, respectively. The cleavage of the C(17)–O(30) bond is, therefore, not stereoelectronically assisted. Similarly, none of the O-30 and O-16 lone-pair orbitals are antiperiplanar to O-35 [Figure 5 (a) and (b), respectively], and the cleavage of the C(17)–O(35) bond is not favoured on stereoelectronic grounds.

The above requirements indicate that when the ortho ester adopts the solid-state conformation (i) (Figure 4), stereoelectronic factors favour hydrolysis *via* the initial cleavage of the C(17)–O(16) bond (Figure 1). A similar investigation of the ortho ester oxygen lone-pair orbital orientations of the conformers (ii) and (iii) indicated that the former will also favour the C(17)–O(16) bond cleavage, but (iii) does not have proper orbital orientation to permit stereoelectronic cleavage of the ortho ester.

Stereoelectronic control of the acid-catalysed hydrolysis of austalide A (**1**) is, therefore, in agreement with the mechanism outlined in Figure 1, and in addition offers an explanation for the apparent absence of alternative reaction pathways (Figures 2 and 3).

It was realised that the assumption that the carbonium ion (b), shown in Figure 1, rapidly recyclises could be tested by hydrolysis of the C-15 *O*-acetyl group in the lactone (**9**). In the event, treatment of the lactone (**9**) with a methanolic solution of

Table. Ortho ester torsion angles in austalide A (**1**)

	Torsion angle[a]
C(14)–O(30)–C(17)–O(16)	321.0°
C(15)–O(16)–C(17)–O(30)	13.2°
C(27)–O(35)–C(17)–O(16)	305.2°
C(27)–O(35)–C(17)–O(30)	63.7°

[a] Calculated from the *X*-ray crystallographic data of austalide A (**1**).

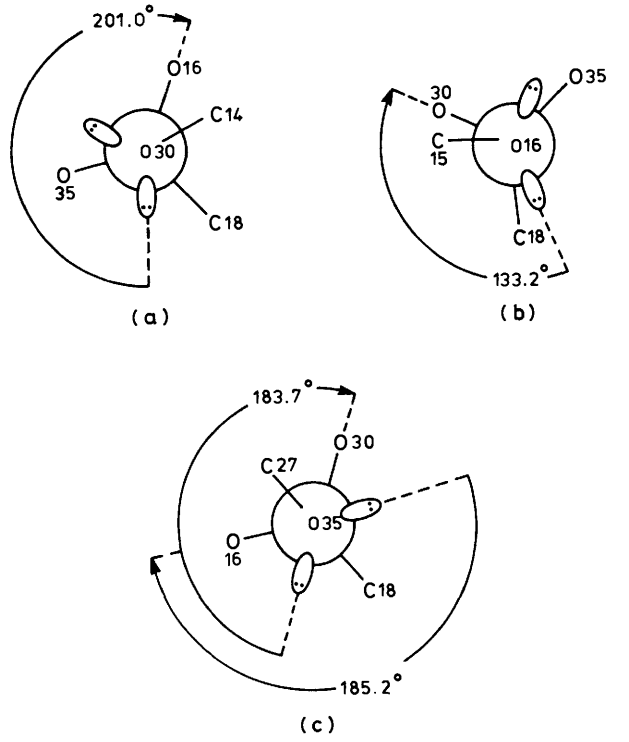


Figure 5. Newman projections of the ortho ester moiety in austalide A (**1**) assuming a solid state conformation. View along the (a) O(30)–C(17), (b) O(16)–C(17), (c) O(35)–C(17) bond

potassium hydroxide followed by acidic work-up gave the hemi-ortho ester (**12**) in high yield. Mass spectrometry showed that only one *O*-acetyl group of (**9**), M^+ 544, is hydrolysed to form the product (**12**), M^+ 502. Analysis of the ABX spin system due to the C-12 and C-13 protons indicated that the C-13 *O*-acetyl group had remained intact. The ^{13}C n.m.r. signal (δ_C 167.79) assigned to C-17 in (**9**) is absent in the spectrum of (**12**), and a new resonance is apparent at δ_C 117.82. This chemical shift compares well with the corresponding shifts of the ortho ester carbon atoms in austalides A—F [(**1**)—(**6**)].[1]

The fact that the C-15 *O*-deacetyl derivative of the lactone (**9**) was not detected in the reaction mixture supports the earlier supposition concerning the rapid recyclisation of the dialkoxy carbonium ion (b) in Figure 1 to give the ortho ester (**1**).

Experimental

For general directions see reference 1.

Perchloric Acid-catalysed Acetylation of Austalide D (**4**).—Austalide D (160 mg) was dissolved in acetic anhydride (5.0 ml), cooled (−78 °C), and treated with perchloric acid (0.05 ml). The mixture was allowed to attain room temperature (15 min), stirred with a sodium hydrogen carbonate–ice mixture for 30 min, and extracted with chloroform (3 × 50 ml). The combined chloroform extracts were washed with water (3 × 50 ml), dried ($MgSO_4$), and evaporated to give a gum. This material was purified by column chromatography on silica gel (20 g) with n-hexane–ethyl acetate (1:1 v/v) as eluant to give austalide C (**3**) (36 mg, 21%), identical with an authentic sample, followed by the δ-*lactone* (**7**) (61 mg, 37%), as a white solid, $[\alpha]_D$ −101.0° (*c* 1.00), $\lambda_{max.}$ 222 and 267 nm (ε 26 300 and 12 600, respectively), $\nu_{max.}$ 1 740 cm^{-1} (Found: M^+, 542.214. $C_{29}H_{34}O_{10}$ requires *M*, 542.215), δ_H 1.170 (3 H, s, 27-H), 1.248 (3 H, s, Me), 1.606 (3 H, s, Me), 1.675 (3 H, s, Me), 1.852 (3 H, s, Me), 1.996 (1 H, dd, *J* 7.4 and 1.4 Hz, 21-H), 2.006 (3 H, s, Me), 2.052 (3 H, s, Me), 2.328 (1 H, dd, *J* 15.9 and 3.5 Hz, 12-H_b), 2.436 (1 H, dd, *J* 15.9 and 2.9 Hz, 12-H_a), 2.839 (1 H, dd, *J* 18.1 and 7.4 Hz, 22-H_b), 2.898 (1 H, dd, *J* 18.1 and 1.4 Hz, 22-H_a), 4.120 (3 H, s, 29-H), 5.101 (2 H, s, 1-H), 5.330 (1 H, dd, *J* 3.5 and 2.9 Hz, 13-H), 5.959 (1 H, d, *J* 9.8 Hz, 19-H), 6.904 (1 H, d, *J* 9.8 Hz, 18-H); δ_C 10.57 Q (C-23), 17.19 Q (C-27), 18.66 T (C-22), 21.55 Q, 23.02 Q, 24.81 Q, 26.06 Q, 26.90 D (C-21), 29.61 Q, 37.12 T (C-12), 48.26 S (C-20), 62.07 Q (C-29), 68.14 T (C-1), 69.73 D (C-13), 74.06 S (C-11), 87.78 S, 89.60 S, 107.68 S, 113.90 S, 113.93 S, 118.72 D (C-19) 146.06 S, 155.43 S, 157.55 S, 158.69 D (C-18), 161.79 S (C-17), 168.08 S, 168.73 S, and 168.94 S; and the δ-*lactone* (**8**) (43 mg, 24%), as a white solid, $[\alpha]_D$ −84.1° (*c* 1.00), $\lambda_{max.}$ 222 and 267 nm (ε 25 800 and 12 100, respectively), $\nu_{max.}$ 1 740 cm^{-1} (Found: M^+, 602.236. $C_{31}H_{38}O_{12}$ requires *M*, 602.236), δ_H 1.140 (3 H, s, 27-H), 1.214 (3 H, s, Me), 1.595 (3 H, s, Me), 1.913 (1 H, d, *J* 8.3 Hz, 21-H), 1.937 (3 H, s, Me), 1.940 (3 H, s, Me), 1.982 (3 H, s, Me), 2.025 (3 H, s, Me), 2.083 (3 H, s, Me), 2.286 (1 H, dd, *J* 16.2 and 4.1 Hz, 12-H_b), 2.516 (1 H, dd, *J* 16.2 and 2.3 Hz, 12-H_a), 2.718 (1 H, d, *J* 20.0 Hz, 18-H_b), 2.969 (1 H, dd, *J* 18.9 and 8.3 Hz, 22-H_b), 3.097 (1 H, dd, *J* 20.0 and 8.5 Hz, 18-H_a), 3.200 (1 H, d, *J* 18.9 Hz, 22-H_a), 4.127 (3 H, s, 29-H), 5.086 (2 H, s, 1-H), 5.305 (1 H, dd, *J* 4.1 and 2.3 Hz, 13-H), and 5.594 (1 H, *J* 8.5 Hz, 19-H); δ_C 10.43 Q (C-23), 13.92 Q (C-27), 19.15 T (C-22), 20.76 Q, 21.32 Q, 22.49 Q, 23.46 Q, 26.89 Q, 27.64 Q, 33.97 T, 36.66 D (C-21), 38.21 T, 44.23 S (C-20), 62.18 Q (C-29), 68.09 T (C-1), 69.20 D, 70.67 D, 74.51 S (C-11), 87.18 S, 88.83 S, 107.92 S, 113.78 S, 114.41 S, 146.03 S, 155.37 S, 157.13 S, 167.76 S (C-17), 167.89 S, 168.61 S, 168.89 S, and 169.88 S.

Perchloric Acid-catalysed Acetylation of Austalide B (**2**).—Austalide B (100 mg) was treated with acetic anhydride and perchloric acid as described above. Similar work-up resulted in a gum that was purified by column chromatography on silica gel (20 g) with n-hexane–ethyl acetate (1:1 v/v) as eluant to give austalide A (**1**) (9 mg, 8%), identical with an authentic sample, followed by the δ-*lactone* (**9**) (102 mg, 88%), a white solid, $[\alpha]_D$ −77.4° (*c* 1.00), $\lambda_{max.}$ 222 and 267 nm (ε 27 100 and 12 800, respectively), $\nu_{max.}$ 1 745 cm^{-1} (Found: M^+, 544.230. $C_{29}H_{36}O_{10}$ requires *M*, 544.231), δ_H 1.138 (3 H, s, Me), 1.210 (3 H, s, Me), 1.636 (3 H, s, Me), 1.879 (3 H, s, Me), 1.979 (3 H, s, Me), 1.989 (3 H, s, Me), 2.044 (1 H, d, *J* 8.0 Hz, 21-H), 2.085 (3 H, s, Me), 2.026—2.223 (2 H, m, 19-H), 2.259 (1 H, dd, *J* 16.3 and 4.2 Hz, 12-H_b), 2.485 (1 H, dd, *J* 16.3 and 2.2 Hz, 12-H_a), 2.567—2.608 (2 H, m, 18-H), 2.845 (1 H, dd, *J* 18.7 and 8.0 Hz, 22-H_b), 2.934 (1 H, d, *J* 18.7 Hz, 22-H_b), 4.128 (3 H, s, 29-H), 5.102 (2 H, s, 1-H), and 5.249 (1 H, dd, *J* 4.2 and 2.2 Hz, 13-H); δ_C 10.46 Q (C-23), 17.56 T (C-22), 19.50 Q (C-27), 21.30 Q, 22.54 Q, 26.67 Q, 27.32 Q, 27.85 T, 27.86 Q, 30.08 T, 36.73 D (C-21), 36.89 T (C-12), 39.95 S (C-20), 62.04 Q (C-29), 68.11 T (C-1), 70.70 D (C-13), 74.53 S (C-11), 87.67 S, 89.69 S, 107.59 S, 113.59 S, 114.92 S, 145.87 S, 155.24 S, 157.69 S, 167.79 S (C-17), 168.70 S, 169.00 S, and 170.30 S.

Hydrogenation of the δ-*Lactone* (**7**).—The δ-lactone (**7**) (5 mg) in ethanol (20 ml) was hydrogenated for 16 h over 10% palladium–carbon (5 mg). Filtration and evaporation of the

ethanol under reduced pressure gave a compound (4 mg, 80%), identical with an authentic sample of the δ-lactone (**9**).

Treatment of Austalide D (**4**) *with Dioxane–Perchloric Acid.*—Aqueous perchloric acid (40%, 0.1 ml) was added to a precooled solution (5 °C) of austalide D (5 mg) in dioxane (10 ml). The reaction mixture was gently heated to 35 °C and stirred for 4 h. Work-up as before gave only starting material (5 mg).

Treatment of Austalide D (**4**) *with Acetic Acid–Perchloric Acid.*—A precooled solution of austalide D (5 mg) in glacial acetic acid (5 ml) was treated with aqueous perchloric acid (40%, 0.1 ml) as described above. Work-up as before gave only starting material (5 mg).

Treatment of Austalide D (**4**) *with Hydrochloric Acid.*—A solution of austalide D (5 mg) in tetrahydrofuran (10 ml) was treated with 0.5M-HCl (0.1 ml) and stirred for 18 h at room temperature. Work-up as before gave only starting material (5 mg).

Alkaline Hydrolysis of the δ-Lactone (**9**).—The δ-lactone (**9**) (90 mg) was hydrolysed with 0.1M-KOH in methanol for 16 h at room temperature. The reaction mixture was acidified (1M-HCl), diluted with water (50 ml), and extracted with chloroform (3 × 50 ml). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The resulting material was recrystallised from n-hexane–chloroform–acetone to give the *hemi-ortho ester* (**12**) (60 mg, 72%) as white prisms, m.p. 198—200 °C, $[\alpha]_D$ −104.5° (*c* 1.00), $\lambda_{max.}$ 222 and 266 nm (ε 24 500 and 11 100, respectively), $\nu_{max.}$ 1 740 cm^{-1} (Found: M^+, 502.218. $C_{27}H_{34}O_9$ requires *M*, 502.220), δ_H 0.974 (3 H, s, 27-H), 1.208 (3 H, s, Me), 1.287 (3 H, s, Me), 1.514 (3 H, s, Me), 1.762—2.079 (4 H, m, 18- and 19-H), 1.965 (3 H, s, Me), 2.031 (3 H, s, Me), 2.142 (1 H, dd, *J* 16.1 and 4.3 Hz, 12-H_b), 2.409 (1 H, d, *J* 8.2 Hz, 21-H), 2.539 (1 H, dd, *J* 16.1 and 2.0 Hz, 12-H_a), 2.844 (1 H, dd, *J* 18.7 and 8.2 Hz, 22-H_b), 2.942 (1 H, dd, *J* 18.7 Hz, 22-H_a), 4.106 (3 H, s, 29-H), 5.069 (1 H, dd, *J* 4.3 and 2.0 Hz, 13-H), and 5.091 (2 H, s, 1-H); δ_C 10.51 Q (C-23), 18.02 T (C-22), 18.11 Q (C-27), 21.14 Q, 25.47 Q, 27.53 Q, 29.33 Q, 29.81 T, 31.04 T, 36.04 D (C-21), 38.04 T (C-12), 40.23 S (C-20), 61.98 Q (C-29), 68.18 T (C-1), 70.90 D (C-13), 75.59 S (C-11), 85.03 S, 86.24 S, 107.42 S, 113.89 S, 115.65 S, 117.82 S (C-17), 145.55 S, 155.40 S, 157.91 S, 169.30 S, and 169.43 S.

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