Ethylidenetetronic Acid and its Derivatives. Condensations with Carbonyl Compounds, leading to Reassignment of Ramigenic Acid from *Penicillium charlesii*

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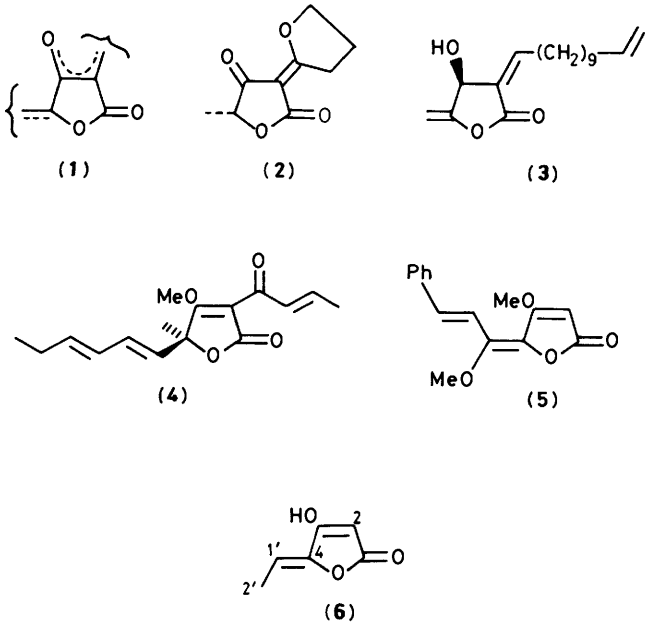
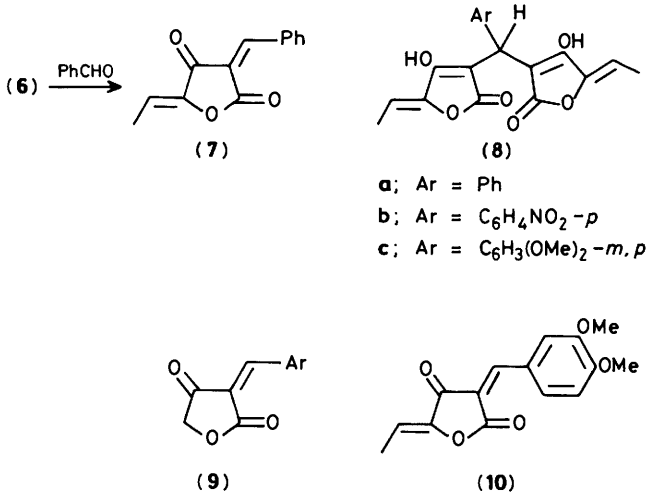
Condensation reactions between ethylidenetetronic acid (**6**) and aryl aldehydes in the presence of weak bases, lead to the 2:1 adducts (**8**); with 3,4-dimethoxybenzaldehyde the 1:1 adduct (**10**) is produced concurrently. Reaction between (**6**) and acetone initially leads to a similar 2:1 adduct *i.e.* (**12**), but on further heating in acetone this adduct disporportionates giving the novel dihydropyran (**13**). The structure of (**13**) was solved by single crystal *X*-ray determination. Comparison of spectral data, and synthesis show that the structure of the analogous compound 'ramigenic acid' isolated from *Penicillium charlesii* should be reassigned as shown in formula (**17b**).

A wide variety of compounds containing the 4-oxyfuran-2-one moiety (**1**) are found in Nature, and many of these members display useful biological properties *e.g.* carlosic acid (**2**),[1] obtusilactone (**3**),[2] aspertetronin (**4**),[3] and ylidenetetronic acids (**5**).[1,4] As a general synthetic entry to molecules within these classes of natural products, we have investigated the carbanion reactivity of ethylidenetetronic acid (**6**) and its derivatives. In this paper we show that condensation reactions between (**6**) and carbonyl compounds leads to a range of interesting 2:1 and 2:2 adducts, which in one instance permits the reassignment of the structure previously given to ramigenic acid isolated from *Penicillium charlesii*. In the accompanying paper, we describe complementary investigations which establish that with selected conditions using appropriate derivatives of (**6**) it is possible to control α-(C-2), γ-(C-4), or ε(C-2′) substitution within (**6**) to produce molecules containing the 4-oxyfuran-2-one substitution patterns found in compounds (**2**), (**3**), (**4**), and (**5**).

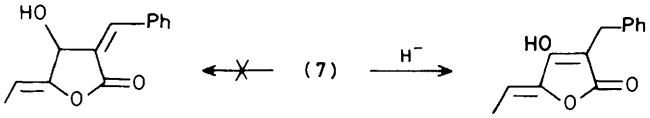
Ethylidenetetronic acid (**6**) is conveniently prepared on large scale by a modification of the procedure described by Fleming and Harley-Mason.[5] It is a molecule in which each carbon atom is functionalised, with the even-numbered centres acting as donors, and the odd-numbered centres acting as acceptor atoms. It was our intention to enhance the donor properties of the C-2(α-), C-4(γ-) and C-2′(ε-) carbon atoms in (**6**) and its derivatives, by the formation of appropriate carbanions, and to exploit their nucleophilicity to provide access to the natural product types (**2**)—(**5**). Thus, aldol condensation at C-2, followed by dehydration would provide 3-ylidenefuran-2,4-diones [*cf.* (**2**)], which by reduction at C-4 would lead to the 4-oxyfuran-2-one system found in obtusilactone (**3**). Similarly aldol condensation at C-2′ could give rise to compounds of the piperolide (**5**) type, whereas the aspertetronin (**4**) substitution pattern would be obtained by methylation at C-4 in (**6**) and its derivatives.

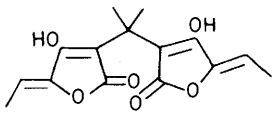
We first examined the condensations between (**6**) and a range of aromatic aldehydes. Thus, condensation of (**6**) with benzaldehyde in the presence of potassium carbonate led to a colourless crystalline solid, whose spectral data supported the structure (**8a**). This 2:1 adduct between (**6**) and benzaldehyde presumably arises *via* facile Michael addition of the ylidenetetronic acid to the initially produced 1:1 adduct (**7**). An analogous product (**8b**) was produced in 98% yield, when 4-nitrobenzaldehyde was condensed with ethylidenetetronic acid in the presence of pyridine. Even with a large excess of the arylaldehyde we were unable to intercept the presumed 1:1 adducts, *e.g.* (**7**) in either of these condensations. Zimmer *et al.*[6]

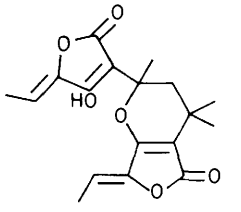




have described the preparation of 1:1 adducts, *e.g.* (**9**), from arylaldehydes and tetronic acid itself, using acid catalysis, but due largely to solubility problems we were unable to use these authors' conditions with the ethylidenetetronic acid (**6**). However, by employing the electron donating 3,4-dimethoxybenzaldehyde in condensation with (**6**), we were able to reduce the Michael acceptor reactivity of the first formed 1:1 adduct [*viz* (**7**)], such that a small amount of the intermediate (**10**) could be separated and characterised. In view of the above observations, an approach to obtusilactone (**3**) using intermediates similar to (**7**) and involving selective 1,2-reduction now seemed impractable; conjugate 1,4- reduction of (**7**) leading to the corresponding tetronic acid (**11**) was likely to compete severely.







We next turned to the condensation reaction between ethylidenetetronic acid and acetone, which took a surprising and interesting course. Thus, dissolution of (**6**) in aqueous acetone at 25 °C resulted in the precipitation of a white solid within 0.5 h. The solid was shown to be the 2:1 bis-tetronic acid adduct (**12**) on the basis of spectral data and precedent from earlier work by Wolff[7] and by Clutterbuck[8] with more simple tetronic acids. When either the bis-tetronic acid (**12**) or ethylidenetetronic acid (**6**) was heated under reflux in ethanolic acetone, a second crystalline product, corresponding to a 2:2 adduct between (**6**) and acetone was produced. The new compound showed three non-equivalent methyl groups attached to sp^3 carbon centres in its ^1H n.m.r. spectrum, and an AB quartet (δ 1.92, 2.56, J 15 Hz) corresponding to a methylene group with non-equivalent hydrogen atoms. The structure of this compound was solved by a single crystal *X*-ray determination, and shown to be the novel dihydropyran (**13**) (see Figure).

Comparison of the structures (**12**) and (**13**) shows immediately that the latter is not derived *via* direct reaction of the former with acetone. It seems likely that the dihydropyran (**13**) is derived from (**12**) through prior dissociation to the 1:1 adduct (**14**) and ethylidenetetronic acid (see Scheme 1). Tandem Michael reaction between (**14**) and its tautomer (**15**) would then lead to the observed product (**13**), although a concerted Diels-Alder reaction involving (**15**) and the electron deficient oxadiene (**14**) cannot be ruled out.

The isolation of (**13**) from condensation between ethylidenetetronic acid and acetone, threw doubt on the structures (**16a**) and (**16b**) assigned by Wolff and Clutterbuck for similar 2:2 adducts produced from tetronic acid and 4-methyltetronic acid respectively.[7,8] Indeed, the adduct (**16b**) has been reported by Clutterbuck *et al*[9] as a natural product, ramigenic acid, isolated with carlic and carlosic acids from *Penicillium charlesii*. This report was later withdrawn however when it was established that the 'natural' product was actually 4-methyltetronic acid; the 2:2 adduct, ramigenic acid, was an artefact of the isolation procedure which used acetone.

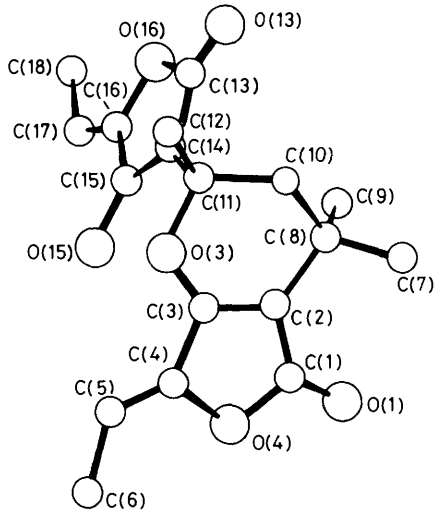
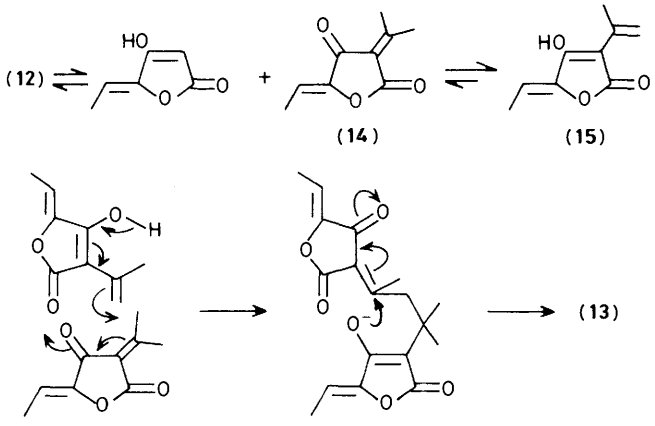
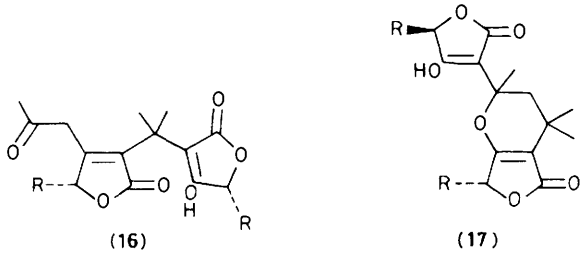


Figure. Crystal structure of (**13**).



Scheme 1.



a; R = H; **b**; R = Me

With our new found information, we have repeated the early work of Wolff and of Clutterbuck and condensed tetronic acid with acetone under their reaction conditions. This has led to a stable crystalline 2:2 adduct identical to that described earlier, which does indeed show spectral properties closely similar to those recorded for the 2:2 adduct (**13**) produced from (**6**). There is no doubt therefore that Clutterbuck's 'ramigenic acid' should be reassigned as shown in formula (**17b**).

Experimental

M.p.s were determined on a Kofler hot-stage apparatus, and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 710B spectrometer, and u.v. spectra were recorded on a Unicam SP800 spectrometer. ^{1}H N.m.r. spectra were determined with a Perkin-Elmer R32 or a 100M. ᶻz Jeol JNP-PS-100 spectrometer, and ^{13}C n.m.r. spectra were recorded on a Bruker WM250 PFT spectrometer; deuteriochloroform was used as solvent with $SiMe_4$ as the internal standard. Bands were singlets except where stated otherwise, and separations between lines (J) are in Hz. Molecular weights were determined from mass spectra, measured with an A.E.I. MS902 spectrometer. All solvents for chromatography were redistilled, and all organic solutions were dried over anhydrous magnesium sulphate.

Ethylidenetetronic acid (**6**) was prepared essentially as described in the literature,[5] except for the following modification. The optimum strength of sodium hydroxide solution used for the cyclisation step, involving the dibromo derivative of diethyl crotonylmalonate, was found to be 3.5—3.7M; this resulted in considerably increased overall yields of the ethylidenetetronic acid.

2,2′-*Benzylidenebis*[4-*ethylidene*-3-*hydroxyfuran*-2(5H)-*one*] (**8a**).—A solution of ethylidenetetronic acid (4-ethylidene-3-hydroxybut-2-enolide) (0.63 g) and benzaldehyde (0.53 g) in dry tetrahydrofuran (50 cm^3) was heated under reflux in the presence of potassium carbonate (0.7 h) for 4 days. The cooled mixture was left at 25 °C for 2 days and then diluted with water (50 cm^3) and acidified with dilute hydrochloric acid. The oil which separated was extracted into ether, and the combined ether extracts were then dried and evaporated to leave the bistetronic acid as an oily solid (1.1 g). Repeated crystallisation from ethanol gave the pure *bis-tetronic acid* (0.42 g) as colourless hexagonal prisms, m.p. 193—4 °C (decomp.), $\lambda_{max.}$(EtOH) 258 (28 000) and 271sh nm (27 000); $\lambda_{max.}$ (basic EtOH) 244 and 309 nm; $\nu_{max.}$(KBr) 1 705, 1 690, and 1 610 cm^{-1}; δ(CD_6CO) 1.88 (d, J 7.7, 2 × :CH*Me*), 5.17 (PhC*H*), 5.77 (q, J 7.7, 2 × :C*H*Me), and 7.25 (br, Ph) (Found: C, 66.8; H, 4.8. $C_{19}H_{16}O_6$ requires C, 67.05; H, 4.7%).

2,2′-(4-*Nitrophenylbenzylidene*)*bis*[4-*ethylidene*-3-*hydroxyfuran*-2(5H)-*one*] (**8b**).—A solution of ethylidenetetronic acid (0.31 g) and 4-nitrobenzaldehyde (1.5 g) in ethanol (20 cm^3) containing pyridine (10 drops) was heated under reflux for 3 days and then evaporated to dryness. The residue was diluted with ethyl acetate and then extracted with sodium hydrogen carbonate solution (× 2). The separated aqueous solution was carefully acidified with concentrated hydrochloric acid and then extracted with ethyl acetate (× 2). Evaporation of the dried ethyl acetate extracts left the crude *bis-tetronic* acid (0.47 g, 98%) as a yellow amorphous solid, m.p. 120—170 °C (decomp.), $\lambda_{max.}$(EtOH) 261nm; $\nu_{max.}$(KBr) 3 600—2 400, 1 720, 1 690, 1 615, 1 522, and 1 355 cm^{-1}; δ 1.96 (d, J 7.5, 2 × :CH*Me*), 5.62 (ArC*H*), 5.93 (q, J 7.5, 2 × :C*H*Me), 7.33 (d, J 8.5, 2 H), and 8.07 (d, J 8.5, 2 H); a small sample was recrystallised from cyclohexane (Found: C, 58.9; H, 4.3; N, 3.56; *m/z* 259.0491; $C_{19}H_{15}NO_8$ requires C, 59.2; H, 3.9; N, 3.6%; $M - C_6H_6O_3$ 259.0481).

2,2′-(3,4-*Dimethoxybenzylidene*)*bis*[4-*ethylidene*-3-*hydroxyfuran*-2(5H)-*one*] (**8c**) *and* 3-(3,4-*Dimethoxybenzylidene*)-5-*ethylidenefuran*-2,4-*dione* (**10**).—A solution of ethylidenetetronic acid (0.7 g) and 3,4-dimethoxybenzaldehyde (4.2 g) in ethanol (125 cm^3) containing pyridine (10 drops) was heated under reflux for 14 h and then evaporated to dryness. The residue was diluted with ether, whereupon an orange-yellow solid (0.19 g) was precipitated. The solid was filtered off and the filtrate was extracted with sodium hydrogen carbonate solution. The separated aqueous solution was acidified with concentrated hydrochloric acid and then extracted with ethyl acetate. Evaporation of the dried ethyl acetate extracts left the *bistetronic acid* (0.51 g, 51%) as a pale orange solid, m.p. > 150 °C (decomp.), and $\lambda_{max.}$(EtOH) 272infl, 259, and 242infl nm; $\nu_{max.}$($CHCl_3$) 3 500—2 500, 1 720, 1 690, and 1 620 cm^{-1}; δ 1.93 (d, J 7.5, 2 × :CH*Me*), 3.72 (OMe), 3.79 (OMe), 5.47 (ArC*H*), 5.83 (q, J 7.5, 2 × C*H*Me), and 6.71 (br, 6 H) (Found: M^+ 400.1171. $C_{21}H_{20}O_8$ requires M 400.1158). A satisfactory solvent for recrystallisation could not be obtained. Recrystallisation of the orange-yellow solid (above) from propan-2-ol gave the corresponding *furanone* as orange needles, m.p. 200—202 °C, $\lambda_{max.}$(EtOH) 426 (20 000), 251sh (15 500), and 230 nm (18 700); $\nu_{max.}$(KBr) 2 920, 1 758, 1 705, 1 653, 1 605, 1 570, 1 555, and 1 505 cm^{-1}; δ 1.92 (d, J 7.5, :CH*Me*), 3.99 (OMe), 4.01 (OMe), 5.99 (q, J 7.5, C*H*Me), 6.95 (d, J 9, 1H), 7.74 (dm, J *ca.* 9, 1 H), 7.94 (br, 1 H), and 8.73 and 8.91 (br, C*H*Ar, *Z*- and *E*-isomers) (Found: C, 65.9; H, 5.3%; M^+, 274.0841. $C_{15}H_{14}O_5$ requires C, 65.7; H, 5.2%; M 274.0841).

2,2′-*Isopropylidenebis*[4-*ethylidene*-3-*hydroxyfuran*-2(5H)-*one*] (**12**).—Water (20 cm^3) was added to a solution of ethylidenetetronic acid (0.25 g) in acetone (5 cm^3) and the solution was left at 25 °C for 0.5 h. Filtration gave the *bistetronic acid* (0.18 g, 62%) as fine white needles, m.p. 162—4 °C, $\lambda_{max.}$(EtOH) 262 nm; $\nu_{max.}$(KBr) 3 300, 3 450—2 200, 1 715, and 1 625 cm^{-1}; δ(CD_6SO) 1.55 (CMe_2), 1.76 (d, J 7.3, 2 × CHMe), and 5.66 (q, J 7.3, 2 × CHMe) (Found: C, 61.6; H, 5.7. $C_{15}H_{16}O_6$ requires C, 61.6; H, 5.5%).

The 2-Dihydropyran-substituted Tetronic Acid (**13**).—A solution of 2,2′-isopropylidenebis[4-ethylidene-3-hydroxyfuran-2(5*H*)-one] (41 mg) in ethanol (9 cm^3) and acetone (3 cm^3) was heated under reflux for 0.5 h and then evaporated to dryness under reduced pressure. A ^{1}H n.m.r. spectrum of the residue showed that it consisted of a mixture of the starting butenolide, ethylidenetetronic acid, and the dihydropyran (**13**) in a ratio of 3:4:6. A similar mixture of products could be obtained when ethylidenetetronic acid was heated in acetone for 0.5 h, whereas prolonged heating (several days) led to only the dihydropyran and ethylidenetetronic acid. Chromatography on silica using benzene–ethyl acetate (1:1) as the eluant gave the dihydropyran (eluted first) which crystallised from benzene as colourless prisms, m.p. 152—157 °C (decomp.), $\lambda_{max.}$ (acidic EtOH) 263.5 (13 000) nm; $\nu_{max.}$($CHCl_3$) 3 580, 3 000, 1 760, 1 690, and 1 640 cm^{-1}; δ 1.2 (Me), 1.35 (Me), 1.92 (d, J 7.5, :CH*Me*), 1.92 (d, J 15, C*H*H), 2.56 (d, J 15, CH*H*), 5.45 (q, J 7.5, :C*H*Me), and 5.62 (q, J 7.5, :C*H*Me) (Found: C, 64.9; H, 5.8. $C_{18}H_{20}O_6$ requires C, 65.05; H, 6.1%).

Crystallographic Analysis.—Crystal data. $C_{18}H_{20}O_6$, M = 332.36, Monoclinic, a = 13.107(5), b = 11.592(3), c = 11.721(3) Å, β = 104.74(3)°, U = 1 722.2 Å^3, Z = 4, D_c = 1.28 g cm^{-3}, F(000) = 704, space group $P2_1/n$, Mo-K_α radiation λ = 0.710 69 Å, μ(Mo-K_α) = 1.04 cm^{-1}.

A crystal of approximate dimensions 0.6 × 0.3 × 0.2 mm was mounted on a Hilger Y290 diffractometer and 23 reflections were used to determine accurate lattice parameters by least squares. Intensity data were collected using a ω—2θ scan for 1° ≤ θ ≤ 25°. A total of 3 033 independent reflections was measured of which 2 130 had $I \geq 3\sigma(I)$ and were considered observed and used in the subsequent refinement. 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.[10] The structure was solved by direct methods using the MULTAN program.[11] Least square refinement including anisotropic thermal parameters for non-hydrogen atoms and

Table 1.

Atom	x/a	y/b	z/c
C(1)	0.326 2(2)	−0.059 4(2)	0.006 3(2)
C(2)	0.312 2(2)	0.032 4(2)	0.082 2(2)
C(3)	0.376 7(2)	0.009 7(2)	0.168 5(2)
C(4)	0.431 2(2)	−0.098 3(2)	0.185 7(2)
C(5)	0.497 0(2)	−0.157 2(2)	0.269 0(3)
C(6)	0.542 4(3)	−0.272 0(3)	0.252 6(4)
C(7)	0.126 0(2)	0.091 9(3)	0.001 0(3)
C(8)	0.238 8(2)	0.133 8(2)	0.055 7(2)
C(9)	0.270 3(3)	0.216 7(3)	−0.030 7(3)
C(10)	0.242 7(2)	0.188 5(2)	0.176 8(2)
C(11)	0.349 9(2)	0.190 3(2)	0.266 6(2)
C(12)	0.338 8(3)	0.227 2(3)	0.387 3(3)
C(13)	0.412 6(2)	0.386 3(2)	0.206 9(2)
C(14)	0.430 2(2)	0.263 9(2)	0.228 2(2)
C(15)	0.522 9(2)	0.240 1(2)	0.204 3(2)
C(16)	0.567 0(2)	0.344 1(2)	0.167 7(2)
C(17)	0.655 3(2)	0.362 7(2)	0.136 1(2)
C(18)	0.691 6(3)	0.476 3(3)	0.102 1(4)
O(1)	0.287 5(1)	−0.076 8(1)	−0.098 1(2)
O(3)	0.393 4(1)	0.072 5(1)	0.286 3(1)
O(4)	0.297 5(1)	−0.138 2(1)	0.069 6(1)
O(13)	0.340 7(2)	0.447 3(1)	0.215 2(2)
O(15)	0.570 5(1)	0.137 9(1)	0.213 8(2)
O(16)	0.496 5(1)	0.432 7(1)	0.171 0(1)
H(5)	0.515(2)	−0.119(2)	0.346(2)
H(6a)	0.515(3)	−0.300(3)	0.169(4)
H(6b)	0.613(5)	−0.271(4)	0.273(5)
H(6c)	0.538(4)	−0.322(4)	0.314(4)
H(7a)	0.120(2)	0.055(2)	−0.075(3)
H(7b)	0.074(2)	0.158(3)	−0.014(3)
H(7c)	0.105(2)	0.035(2)	0.056(2)
H(9a)	0.268(2)	0.179(3)	−0.105(3)
H(9b)	0.342(2)	0.246(2)	−0.002(2)
H(9c)	0.220(3)	0.284(3)	−0.045(3)
H(10a)	0.216(2)	0.268(2)	0.167(2)
H(10b)	0.198(2)	0.142(2)	0.214(2)
H(12a)	0.285(2)	0.173(2)	0.412(2)
H(12b)	0.408(2)	0.216(2)	0.447(2)
H(12c)	0.317(3)	0.307(3)	0.384(3)
H(17)	0.700(2)	0.296(2)	0.137(2)
H(18a)	0.638(3)	0.534(3)	0.104(3)
H(18b)	0.699(3)	0.476(3)	0.023(4)
H(18c)	0.763(4)	0.494(4)	0.147(4)
H(015)	0.620(3)	0.134(3)	0.174(3)

isotropic refinement of hydrogen atoms located in a difference Fourier synthesis terminated at R 0.0417 (R_w 0.0448) with maximum δ/σ 0.1. A final difference map showed no features in excess of 0.2 e Å^{-3}. Final atomic co-ordinates are listed in Table 1. Temperature factors are listed in a Supplementary Publication [SUP No. 56317 (3 pp.)].* Structure factors are available from the Editorial Office on request.

Bond lengths and angles are listed in Tables 2 and 3 together with their standard deviations. These mainly adopt expected values. An exception occurs in both of the lactone rings whose strained nature imposes exocyclic bond angles in excess of 130° at the sp^2 hybridised carbon. Similar angles were found in the only previous determined structures containing this ring system.[12] Both lactone rings are completely planar (max. δ 0.009 Å) while the dihydropyran adopts the expected half chair conformation. Curiously the conformation about the C(11)–C(14) bond is eclipsed [O(3)-C(11)-C(14)-C(15) torsion angle 4.5°] placing O(3) in the lactone ring plane and reducing the O(3)–O(15) distance to only 2.773 Å. An intramolecular hydrogen bond is not formed, however, as the hydrogen atom H(15) was located in a difference map forming an intermolecular hydrogen bond [O(15)-O(1) (1 − x, −y, −z) 2.662 Å, see Tables 2 and 3].

Table 2. Bond lengths (Å)

C(1)	C(2)	1.429(3)	C(11)	C(14)	1.509(3)
C(1)	O(1)	1.216(3)	C(11)	O(3)	1.476(3)
C(1)	O(4)	1.380(3)	C(13)	C(14)	1.449(3)
C(2)	C(3)	1.342(3)	C(13)	O(13)	1.202(3)
C(2)	C(8)	1.501(3)	C(13)	O(16)	1.383(3)
C(3)	C(4)	1.446(3)	C(14)	C(15)	1.343(3)
C(3)	O(3)	1.329(3)	C(15)	C(16)	1.449(3)
C(4)	C(5)	1.317(3)	C(15)	O(15)	1.330(3)
C(4)	O(4)	1.398(3)	C(16)	C(17)	1.320(3)
C(5)	C(6)	1.490(4)	C(16)	O(16)	1.389(3)
C(7)	C(8)	1.533(3)	C(17)	C(18)	1.489(4)
C(8)	C(9)	1.527(3)			
C(8)	C(10)	1.543(3)	O(15)	O(1′)	2.662(4)
C(10)	C(11)	1.526(3)	O(15)	H(15)	0.89(3)
C(11)	C(12)	1.520(3)	O(1′)	H(15)	1.80(3)

Table 3. Bond angles (°)

C(2)	C(1)	O(1)	131.5(2)	C(12)	C(11)	C(14)	111.0(2)
C(2)	C(1)	O(4)	109.6(2)	C(12)	C(11)	O(3)	103.8(2)
O(1)	C(1)	O(4)	118.9(2)	C(14)	C(11)	O(3)	107.3(2)
C(1)	C(2)	C(3)	106.4(2)	C(14)	C(13)	O(13)	131.0(2)
C(1)	C(2)	C(8)	129.2(2)	C(14)	C(13)	O(16)	109.2(2)
C(3)	C(2)	C(8)	124.4(2)	O(13)	C(13)	O(16)	119.8(2)
C(2)	C(3)	C(4)	110.3(2)	C(11)	C(14)	C(13)	120.8(2)
C(2)	C(3)	O(3)	128.4(2)	C(11)	C(14)	C(15)	133.1(2)
C(4)	C(3)	O(3)	121.3(2)	C(13)	C(14)	C(15)	106.2(2)
C(3)	C(4)	C(5)	131.7(2)	C(14)	C(15)	C(16)	109.9(2)
C(3)	C(4)	O(4)	105.8(2)	C(14)	C(15)	O(15)	126.6(2)
C(5)	C(4)	O(4)	122.4(2)	C(16)	C(15)	O(15)	123.5(2)
C(4)	C(5)	C(6)	125.1(3)	C(15)	C(16)	C(17)	131.5(2)
C(2)	C(8)	C(7)	109.8(2)	C(15)	C(16)	O(16)	106.8(2)
C(2)	C(8)	C(9)	111.2(2)	C(17)	C(16)	O(16)	121.6(2)
C(2)	C(8)	C(10)	105.2(2)	C(16)	C(17)	C(18)	125.6(3)
C(7)	C(8)	C(9)	108.5(2)	C(3)	O(3)	C(11)	113.6(2)
C(7)	C(8)	C(10)	108.5(2)	C(1)	O(4)	C(4)	107.9(2)
C(9)	C(8)	C(10)	113.6(2)	C(13)	O(16)	C(16)	107.9(2)
C(8)	C(10)	C(11)	116.7(2)				
C(10)	C(11)	C(12)	110.9(2)	C(15)	O(15)	H(O15)	112.(2)
C(10)	C(11)	C(14)	113.1(2)	O(15)	H(15)	O(1′)	161.(3)
C(10)	C(11)	O(3)	110.3(2)				

2,2′-*Isopropylidenebis*[3-*hydroxyfuran*-2(5H)-*one*] (*J. Buck*).—Acetone (20 cm^3) was added to a solution of tetronic acid [3-hydroxyfuran-2(5*H*)-one] (1 g) in ethanol (20 cm^3) and the resulting solution was heated under reflux for 0.5 h and then evaporated to approximately 15 cm^3. The solution was cooled in ice whereupon the title bis-tetronic acid (0.44 g, 91%) formed white crystals, m.p. 193—194 °C (lit.,[7] m.p. 200—201 °C), $\nu_{max.}$(Nujol) 2 720, 1 710, and 1 675 cm^{-1}; δ(CD_6SO) 1.56 (CMe_2) and 4.52 (4 H) (Found: C, 55.0; H, 5.2. Calc. for $C_{11}H_{12}O_6$: C, 55.0; H, 5.0%).

The 2-*Dihydropyran-substituted Tetronic Acid* (**17a**) (*J. Buck*).—A suspension of 2,2′-isopropylidenebis[3-hydroxyfuran-2(5*H*)-one] (0.5 g) in ethanol (15 cm^3) and acetone (15 cm^3) was heated under reflux until all of the solid had disappeared (*ca.* 18 h). The solution was then evaporated to dryness to leave a solid residue. Crystallisation from methanol gave the *dihydropyran* (0.41 g, 70%) as colourless crystals, m.p.

* For details of the Supplementary Publications Scheme see Instructions for Authors (1985), *J. Chem. Soc., Perkin Trans 1*, 1985, Issue 1.

164—165 °C (Wolff and Schimpff[7] quote m.p. 120 °C), $\nu_{max.}$(Nujol) 3 280, 1 725, 1 675, and 1 655 cm^{-1}; δ (CD_3OD) 1.09 (Me), 1.34 (Me), 1.67 (Me), 1.69 (d, *J* 15, C*H*H), 2.63 (d, *J* 15, CH*H*) 4.64 (CH_2), 4.74 (CH_2), and 5.01 (OH) (Found: C, 56.4, H, 6.3. $C_{14}H_{16}O_6$ requires C, 56.4; H, 6.0%).

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