Structure and Synthesis of the First Flavonoid- and Stilbene-related But-2-enolides

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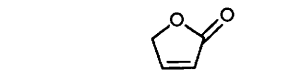
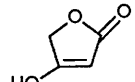
The structures of the first flavonoid- and stilbene-related but-2-enolides [furan-2(5*H*)-ones] have been established as 3-(2,4-dihydroxyphenyl)-4-(4-hydroxybenzyl)but-2-en-4-olide and 3-(3,5-dihydroxystyryl)-4-methoxycarbonylmethylbut-2-en-4-olide, respectively. Confirmation of the structure of the hydroxybenzyl product and hence demonstration of its relationship to the flavonoids was achieved by intramolecular aldol-type reaction of an α-acetoxydihydrochalcone. 3-(3,5-Dihydroxystyryl)-4-methoxycarbonylmethylbut-2-enolide presumably represents a degradation product of 3,3',4,5'-tetrahydroxystilbene.

The significance of the but-2-enolide [furan-2(5*H*)-one] (**1**) and tetronic acid (**2**) ring systems as structural features in a wide range of biologically important natural products has prompted considerable research into the chemistry of these metabolites.[1–3] We now report on the structure and synthesis of 3-(2,4-dihydroxyphenyl)-4-(4-hydroxybenzyl)but-2-en-4-olide (**3**), the first member of the flavonoid-related but-2-enolides, and on the tentative structure of 3-(3,5-dihydroxystyryl)-4-methoxycarbonylmethylbut-2-en-4-olide (**5**), which exhibits some structural resemblance to the stilbene class of natural products.



(1)



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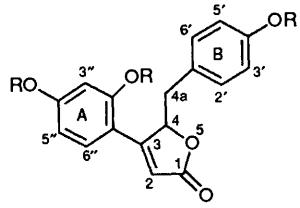
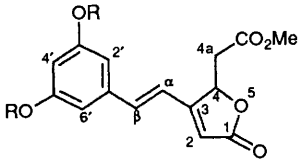


(3) R = H
(4) R = Ac

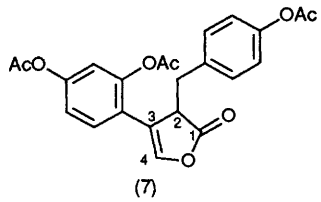


(5) R = H
(6) R = Ac

Results and Discussion

The acetone extract of the heartwood of *Pericopsis elata*† (Harms.),[4] the leaves, root, and bark of which are used in traditional African medicinal preparations,[5] contains a variety of phenolic metabolites, *e.g.* isoflavonoids,[5,6] α-methyldeoxybenzoins,[5] flavanones,[5] stilbenes,[5] and α-hydroxydihydrochalcones.[7,8] These compounds are accompanied by known chalcones,‡ isoflavanones,‡ pterocarpans‡ and the novel but-2-en-4-olides (**3**) and (**5**). Owing to the complexity of the phenolic mixture, compounds (**3**) and (**5**) were purified and identified as their peracetates (**4**) and (**6**).

The aromatic region of the 300 MHz ^{1}H NMR spectrum of the racemic but-2-enolide (**4**) ($C_{23}H_{20}O_8$) in $CDCl_3$ exhibited an ABX-pattern (δ 7.30, d, *J* 9.5 Hz; 7.12, dd, *J* 2.3 and 9.5 Hz; δ 7.11, d, *J* 2.3 Hz) reminiscent of a 2,4-disubstituted A-ring, and an AA'BB'-system (δ 7.03, 6.92, both d, *J* 8.8 Hz) characteristic of a *para*-substituted B-ring. Besides three aromatic acetoxy signals (δ 2.32, 2.26, 2.23), the 'aliphatic' region also displayed an ABMX-system (δ 2.83, dd, *J* 7.0 and 15.0 Hz; δ 3.18 dd, *J* 4.0 and 15.0 Hz; δ 5.66, ddd, *J* 1.6, 4.0, and 7.0 Hz; δ 6.19, d, *J* 1.6 Hz). The chemical shift (δ 6.19) and coupling constant (1.6 Hz) of the X-spin of this system strongly indicated an allylic connection with the methine proton. Spin-decoupling experiments, corroborated by a ^{1}H COSY, demonstrated additional long-range coupling of the presumed vinylic proton with 6-H-(A), and a benzylic relationship of the methylenic AB-spins with 2- and 6-H(B). When taken in conjunction with the presence of an additional ester-type carbonyl in the ^{13}C NMR spectrum and a molecular mass of 424, the ^{1}H NMR features are consistent with either the 3,4-disubstituted but-2-enolide (**4**) or the 2,3-disubstituted but-3-enolide (**7**). The carbonyl absorption (ν_{max} 1 763 cm^{-1}) in the IR spectrum ($CHCl_3$) of the natural product derivative conforms to values reported[9] for α,β-unsaturated lactones of type (**4**), in contrast to absorption in the 1 780–1 800 cm^{-1} region for the but-3-enolides.[10]



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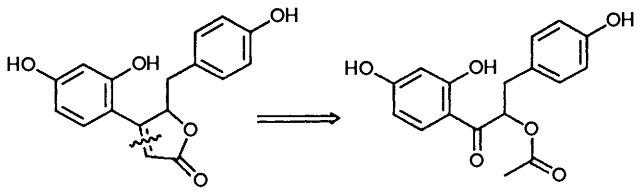
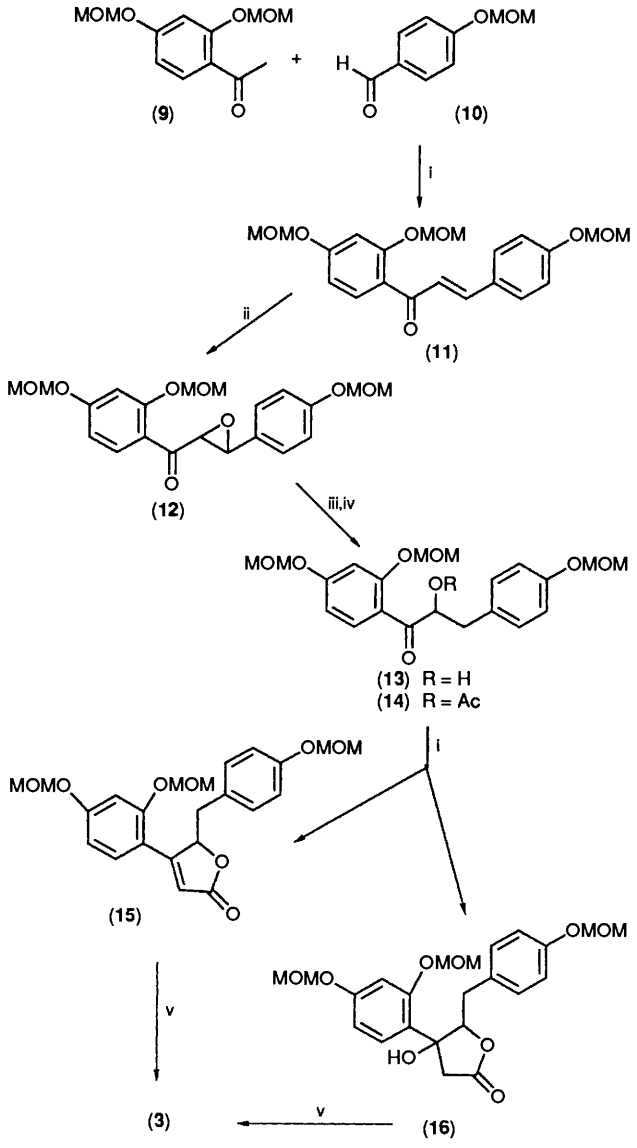


(3) (8)

The close structural resemblance of butenolide (**3**) and the *O*-acetyl derivative (**8**) of the co-existing[8] α,2',4,4'-tetra-

† Previously known as *Afrormosia elata* (Harms.).
‡ To be published elsewhere.

hydroxydihydrochalcone, indicated by the simple disconnection (3) ⇒ (8), prompted structural confirmation of metabolite (3) *via* the synthetic sequence outlined in Scheme 1. Thus,

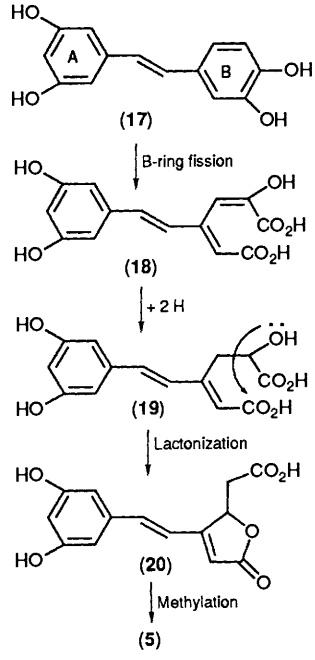


Scheme 1. *Reagents and conditions:* i, LDA, THF, room temp.; ii, H_2O_2, aq. NaOH, MeOH; iii, H_2/Pd–$BaSO_4$, EtOH; iv, Ac_2O–pyridine; v, 3M-HCl, MeOH, heat.

condensation of the *O*-protected acetophenone (**9**) and benzaldehyde (**10**) with lithium di-isopropylamide (LDA) in tetryhydrofuran (THF) afforded the chalcone (**11**), which was converted into the epoxide (**12**) with alkaline hydrogen peroxide.[11] Hydrogenation of the oxirane (**12**) over palladium–barium sulphate[12] in ethanol gave the α-hydroxydihydrochalcone (**13**) and, following acetylation, the acetyl derivative (**14**). This *O*-protected acyloin with its active methyl protons was susceptible to intramolecular aldol-type condensation[2] with LDA in THF, yielding a mixture of the 3,4-disubstituted dihydrotetronic acid (**16**) (41%)* and the but-2-en-4-olide (**15**) (8%).* Under acidic conditions the dihydrotetronic acid (**16**) was deprotected and dehydrated simultaneously to give the butenolide (**3**) (76%),* the peracetate of which was identical with the same derivative of the natural product by comparison of ^{1}H NMR (Table) and IR data. Proof against butenolide (**4**) being an artefact of the acetylation of α,2′,4,4′-tetrahydroxydihydrochalcone was provided by treatment of this tetrol with acetic anhydride–pyridine for 48 h at room temperature which gave the tetra-*O*-acetyl derivative as the only product, thus indicating the inability of pyridine to abstract a methyl proton from the acetyl group.

The ^{1}H NMR spectrum of compound (**6**) ($C_{19}H_{18}O_8$) in $CDCl_3$ exhibited a 'heterocyclic' ABMX-system (δ 2.53, dd, *J* 8.5 and 16.5 Hz; δ 2.90, dd, *J* 3.5 and 16.5 Hz; δ 5.58, ddd, *J* 1.5, 3.5, and 8.5 Hz; δ 6.03, d, *J* 1.5 Hz) very similar to that observed for the butenolide derivative (**4**). Presence of a 3,5-diacetoxystyryl moiety was indicated by an aromatic A_2M-system (δ 7.06, d, *J* 2.0 Hz, 2 H; δ 6.86, t, *J* 2.0 Hz), an AB-pattern (δ 6.85 and 6.77, both d, *J* 16.5 Hz) reminiscent of a *trans*-vinylic system, and two aromatic acetoxy signals (δ 2.23, s, 6 H). A spin-decoupling experiment again confirmed an allylic connection between the protons at δ 6.03 and 5.58, and also long-range coupling of the proton at δ 6.03 and the vinylic protons. A single methoxy resonance (δ 3.69) in association with four ester-type carbonyl resonances (δ_C 171.60, 169.55, 168.69, and 162.95) in the ^{13}C NMR spectrum of compound (**6**) strongly indicated replacement of the B-ring in butenolide (**4**) by a methyl carboxylate group in the former compound. Collectively the ^{1}H and ^{13}C NMR features are compatible with a 3-(3,5-diacetoxystyryl)-4-methoxycarbonylmethylbut-2-en-4-olide structure for the *O*-acetyl derivative (**6**) of this novel metabolite.

The number of carbon atoms, excluding the methyl group of the ester, in the but-2-enolide (**5**) corresponds to that of stilbenes. When taken in conjunction with the presence of a styryl moiety, exhibiting the characteristic 3,5-dioxygenated A-ring of naturally occurring stilbenes, such a corresponding number of carbon atoms presumable indicates that butenolide (**5**) may be regarded as a degradation product[13,14] of the co-existing[5] 3,3′,4,5′-tetrahydroxystilbene† (**17**). The *ortho*-dihydroxy functionality may be oxidatively dissimilated by bond fission[15] to produce a *cis-cis*-muconic acid derivative (**18**). Reduction of the enol system in compound (**18**) to the dihydromuconic acid derivative (**19**) followed by lactonization



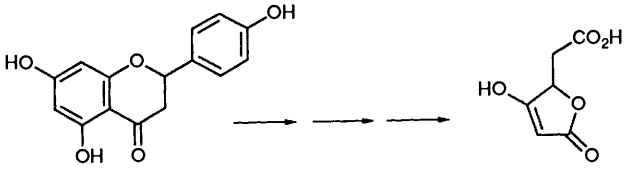
Scheme 2. Proposed route to the formation of the but-2-en-4-olide (**5**).

* See Table for ^{1}H NMR data.

† Systematic nomenclature, giving lowest locants to unprimed substituents.

Table. ^{1}H NMR peaks of but-2-enolides (**3**), (**4**), and (**15**) and the dihydrotetronic acid (**16**) in $CDCl_3$ (297 K) at 300 MHz. Splitting patterns and *J*-values (Hz) are given in parenthesis.

Ring	Proton	(3)	(4)	(15)	(16)
A	3	6.59 (d, 2.2)	7.11 (d, 2.3)	6.90 (d, 2.1)	6.85 (d, 2.5)
	5	6.52 (dd, 2.2, 8.4)	7.12 (dd, 2.3, 9.5)	6.78 (dd, 2.1, 9.0)	6.69 (dd, 2.5, 8.5)
	6	7.40 (d, 8.4)	7.30 (d, 9.5)	7.24 (d, 9.0)	7.28 (d, 8.5)
B	2/6	6.92 (d, 8.5)	7.03 (d, 8.8)	6.95 (d, 9.0)	7.12 (d, 8.7)
	3/5	6.67 (d, 8.5)	6.92 (d, 8.8)	6.86 (d, 9.0)	6.91 (d, 8.7)
C	2	6.17 (d, 1.5)	6.19 (d, 1.6)	6.18 (d, 1.8)	3.38 (d, 17.3), 2.80 (d, 17.3)
	4	5.85 (ddd, 1.5, 3.4, 6.7)	5.66 (ddd, 1.6, 4.0, 7.0)	5.78 (ddd, 1.8, 3.6, 7.0)	5.01 (dd, 3.0, 9.5)
	4a-H_2	3.23 (dd, 3.4, 15.5), 2.74 (dd, 6.7, 15.5)	3.18 (dd, 4.0, 15.0), 2.83 (dd, 7.0, 15.0)	3.21 (dd, 3.6, 15.0), 2.79 (dd, 7.0, 15.0)	3.11 (dd, 9.5, 15.0), 2.86 (dd, 3.0, 15.0)
	OH/OAc	9.50, 9.04, 8.17 (each br s)	2.32, 2.26, 2.23 (each s)		
	CH_2OMe			5.23, 5.22, 5.20, 5.18, 5.12, 5.09 (each d, 7.0)	5.23, 5.18, 5.13, 5.10 (each d, 7.0), 5.15 (s)
	CH_2O*Me*			3.50, 3.444, 3.440 (each s)	3.46, 3.440, 3.435 (each s)



(21) (22)

would then give the but-2-enolide (**20**) which may be methylated to afford metabolite (**5**). Although the sequence in Scheme 2 is speculative, the tetronic acid (**22**) has been shown[16] to be a catabolite of the peroxidatic degradation of the flavanone naringenin (**21**), thus giving credence to the proposed degradation steps for the tetrahydroxystilbene (**17**).

Experimental

^{1}H (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were recorded at 297 K on a Bruker AM-300 spectrometer, for solutions in $CDCl_3$, with the solvent signal as reference. Mass spectral data were obtained with a Kratos MS80 instrument, and IR data were obtained for solutions in $CHCl_3$ or CCl_4 on a Hitachi 270–50 instrument. Preparative plates (PLC), 20 × 20 cm, Kieselgel PF_{254} (1.0 mm) were air dried and used without prior activation. Column chromatography was on Sephadex LH-20 in ethanol or Kieselgel 60 (Merck) in columns of various sizes and at differing flow rates (to be specified in each instance). Acetylations were performed with acetic anhydride–pyridine at ambient temperature. Evaporations were done under reduced pressure at *ca.* 60 °C in a rotary evaporator.

Extraction and Fractionation of Heartwood Components of P. elata.—Heartwood drillings (10 kg) were successively extracted with hexane (3 × 18 l, 24 h for each extraction) and acetone (3 × 18 l, 24 h) at room temperature. Evaporation of the combined acetone extract afforded a dark-brown powder (40 g), which was subjected to column chromatography on Sephadex LH-20 (120 × 5 cm column; flow rate 0.5 ml min^{-1}) to give the following fractions: 1 [Relative retention time 34–68 h (0.13 g)], 2 [$t_{R\,rel}$ 68–110 h (0.33 g)], 3 [$t_{R\,rel}$ 110–156 h (0.09 g)], 4 [$t_{R\,rel}$ 156–205 h (1.92 g)], 5 [$t_{R\,rel}$ 205–258 h (16.55 g)], 6 [$t_{R\,rel}$ 258–301 h (2.09 g)], 7 [$t_{R\,rel}$ 301–344 h (2.81 g)], 8 [$t_{R\,rel}$ 344–390 h (4.99 g)], 9 [$t_{R\,rel}$ 390–437 h (4.91 g)], 10 [$t_{R\,rel}$ 437–471 h (1.57 g)], 11 [$t_{R\,rel}$ 471–509 h (0.87 g)], and 12 [$t_{R\,rel}$ 509–600 h (1.28 g)].

Rechromatography of a portion of fraction 6 (2 g) by PLC in benzene–acetone (8:2) afforded eight subfractions, 6.1 [R_F 0.76 (300 mg)], 6.2 [R_F 0.69 (43 mg)], 6.3 [R_F 0.57 (100 mg)], 6.4 [R_F 0.48 (52 mg)], 6.5 [R_F 0.40 (80 mg)], 6.6 [R_F 0.34 (20 mg)], 6.7 [R_F 0.24 (2 mg)], and 6.8 [R_F 0.14 (60 mg)]. Acetylation of fraction 6.8 (60 mg), subsequent purification by PLC in benzene–acetone (8:2), and crystallization from chloroform gave 4-(4-*acetoxybenzyl*)-3-(2,4-*diacetoxyphenyl*)-*but-2-en-4-olide* (**4**) as light yellow needles (22 mg), m.p. 151–153 °C (Found: C, 65.0; H, 4.8. $C_{23}H_{20}O_8$ requires C, 65.1; H, 4.7%); ^{1}H NMR (Table); δ_C 171.9, 169.2, 168.3, 167.9, 161.9, 152.6, 149.6, 148.7, 132.0, 130.5, 129.3, 121.5, 120.8, 119.7, 118.6, 117.7, 82.7, 38.2, 21.3, 21.2, and 21.1; *m/z* 424 (100%, M^+), 396 (17), 382 (98), 364 (27), 340 (20), 296 (20), 272 (20), 237 (27), 192 (13), 149 (83), and 107 (25); ν_{max} 1 763 cm^{-1} (C=O).

Fraction 8 (4.99 g) from the initial fractionation was re-subjected to column chromatography on silica, with benzene–acetone (8:2) (60 × 3 cm column; flow rate 0.5 ml min^{-1}) to give 6 subfractions, 8.1 [$t_{R\,rel}$ 19–40 h (200 mg)], 8.2 [$t_{R\,rel}$ 40–55 h (480 mg)], 8.3 [$t_{R\,rel}$ 55–68 h (352 mg)], 8.4 [$t_{R\,rel}$ 68–81 h (480 mg)], 8.5 [$t_{R\,rel}$ 81–98 h (277 mg)], and 8.6 [$t_{R\,rel}$ 98–150 h (210 mg)]. Acetylation of fraction 8.5 followed by PLC in hexane–acetone–ethyl acetate (65:20:15) gave 3-(3,5-*diacetoxystyryl*)-4-*methoxycarbonylmethylbut-2-en-4-olide* (**6**) as a light yellow oil (15 mg) (Found: C, 61.0; H, 4.9. $C_{19}H_{18}O_8$ requires C, 60.9; H, 4.8%); δ_H 7.06 (d, *J* 2.0 Hz, 2′- and 6′-H), 6.86 (t, *J* 2.0 Hz, 4′-H), 6.85 (d, *J* 16.5 Hz, β-H), 6.77 (d, *J* 16.5 Hz, α-H), 6.03 (d, *J* 1.5 Hz, 2-H), 5.58 (ddd, *J* 1.5, 3.5, and 8.5 Hz, 4-H), 2.90 (dd, *J* 3.5 and 16.5 Hz, 4a-H), 2.53 (dd, *J* 8.5 and 16.5 Hz, 4a-H), 3.69 (s, CO_2Me), and 2.23 (s, 2 × OAc); δ_C 171.6, 169.6, 168.7, 162.9, 151.4, 136.8, 136.5, 119.6, 117.6, 117.1, 116.8, 77.9, 52.4, 39.0, and 21.2; *m/z* 374 (23%, M^+), 332 (21), 304 (20), 290 (51), 288 (37), 272 (20), 262 (41), 258 (34), 247 (19), 246 (100), 217 (34), 212 (34), 203 (69), 189 (69), 173 (61), and 161 (26).

2′,4,4′-*Tris*(*methoxymethoxy*)*chalcone* (**11**).—To a solution of LDA [prepared *in situ* by the addition of BuLi (4.56 ml of a 15% solution in hexane) to di-isopropylamine (1.6 ml)] in dry THF (10 ml) was added a solution of 2,4-bis(methoxymethoxy)-acetophenone (**9**)[8] (2.14 g) in dry THF (10 ml) and the mixture was stirred at ambient temperature under N_2 for 15 min. A solution of 4-methoxymethoxybenzaldehyde (**10**)[12] (2.0 g) in THF (5 ml) was added and the mixture was stirred for a further 14 h. Ice–water (100 ml) was added, the reaction mixture was acidified with 3M-HCl, and the crude chalcone was extracted with diethyl ether (3 × 100 ml). The combined extracts were washed successively with water (50 ml) and saturated aq. $NaHCO_3$ (50 ml) and dried (Na_2SO_4) before evaporation of the solvent. PLC (hexane–benzene–acetone, 5:4:1) gave the *chalcone* (**11**) (R_F 0.3) as a yellow oil (2.0 g, 58%) (Found: M^+, 388.1520. $C_{21}H_{24}O_7$ requires *M*, 388.1515); δ_H 7.69 (d, *J* 8.5 Hz, 6′-H), 7.60 (d, *J* 15.5 Hz, β-H), 7.51 (d, *J* 8.9 Hz, 2- and 6-H), 7.33 (d, *J* 15.5 Hz, α-H), 7.03 (d, *J* 8.9 Hz, 3- and 5-H), 6.83 (d, *J* 2.1 Hz, 3′-H), 6.75 (dd, *J* 2.1 and 8.5 Hz, 5′-H), 5.22,

5.20, and 5.19 (each s, 3 × OCH_2OMe), and 3.43 (×2) and 3.42 (each s, 3 × OCH_2OMe).

2',4,4'-Tris(methoxymethoxy)chalcone Epoxide (**12**).—Epoxidation[11] (2 h) of the chalcone (**11**) (2.0 g) in MeOH (100 ml) with alkaline H_2O_2 [1M-NaOH solution (10 ml), 6% (w/v) aq. H_2O_2 (30 ml)] gave the epoxide (**12**) (R_F 0.4) as white needles after PLC (hexane–benzene–acetone, 5:4:1; ×2) and crystallization from ethanol–acetone, m.p. 94 °C (lit.,[17] 95 °C); δ_H 7.81 (d, *J* 8.9 Hz, 6'-H), 7.26 (d, *J* 9.0 Hz, 2- and 6-H), 7.02 (d, *J* 9.0 Hz, 3- and 5-H), 6.75 (d, *J* 2.3 Hz, 3'-H), 6.73 (dd, *J* 2.3 and 8.9 Hz, 5'-H), 5.17 and 5.16 (each s, 2 × OCH_2OMe), 4.89 (d, *J* 7.0 Hz) and 4.81 (d, *J* 7.0 Hz) (together OCH_2OMe), 4.27 (d, *J* 2.0 Hz, α-H), 3.91 (d, *J* 2.0 Hz, β-H), and 3.45, 3.44, and 3.10 (each s, OCH_2OMe).

α-Hydroxy-2',4,4'-tris(methoxymethoxy)dihydrochalcone (**13**).—Catalytic hydrogenation[12] (1.5 h) of the chalcone epoxide (**12**) (1.2 g) in EtOH (70 ml) over Pd–$BaSO_4$[18] (400 mg) followed by PLC (chloroform–acetone, 97:3) gave the *α-hydroxydihydrochalcone* (**13**) (R_F 0.3) as a yellow oil (1.07 g, 88%) (Found: M^+ 406.1615. $C_{21}H_{26}O_8$ requires *M*, 406.1620); δ_H 7.82 (d, *J* 8.9 Hz, 6'-H), 7.05 (d, *J* 8.5 Hz, 2- and 6-H), 6.90 (d, *J* 8.5 Hz, 3- and 5-H), 6.86 (d, *J* 2.1 Hz, 3'-H), 6.77 (dd, *J* 2.1 and 8.9 Hz, 5'-H), 5.39–5.31 (m, α-H), 5.30 (d, *J* 7.0 Hz) and 5.22 (d, *J* 7.0 Hz) (together 2'-OCH_2OMe), 5.21 and 5.12 (each s, 2 × OCH_2OMe), 3.89 (d, *J* 6.6 Hz, α-OH), 3.48 (×2) and 3.44 (each s, 3 × OCH_2OMe), 3.10 (dd, *J* 3.9 and 14.0 Hz, β-H), and 2.68 (dd, *J* 7.0 and 14.0 Hz, β-H).

α-Acetoxy-2',4,4'-tris(methoxymethoxy)dihydrochalcone (**14**).—Acetylation of the α-hydroxydihydrochalcone (**13**) (1.0 g) gave the acetate (**14**) (R_F 0.3; hexane–benzene–acetone, 5:4:1) as a white solid (1.05 g, 95%), m.p. 116 °C; δ_H 7.83 (d, *J* 8.8 Hz, 6'-H), 7.14 (d, *J* 8.8 Hz, 2- and 6-H), 6.94 (d, *J* 8.8 Hz, 3- and 5-H), 6.84 (d, *J* 2.3 Hz, 3'-H), 6.74 (dd, *J* 2.3 and 8.8 Hz, 5'-H), 6.16 (dd, *J* 3.0 and 9.9 Hz, α-H), 5.31 (d, *J* 7.0 Hz) and 5.25 (d, *J* 7.0 Hz) (together 2'-OCH_2OMe), 5.19 and 5.13 (each s, 2 × OCH_2OMe), 3.48, 3.47, and 3.46 (each s, 3 × OCH_2OMe), 3.15 (dd, *J* 3.0 and 15.0 Hz, β-H), and 2.88 (dd, *J* 9.9 and 15.0 Hz, β-H); *m/z* 448 (M^+, 2%); $\nu_{max}(CHCl_3)$ 1 740 and 1 680 (C=O), and 1 605 cm^{-1}.

Aldol-type Condensation of α-Acetoxy-2',4,4'-tris(methoxymethoxy)dihydrochalcone (**14**).—To a solution of LDA [prepared *in situ* by the addition of BuLi (0.2 ml of a 15% solution in hexane) to di-isopropylamine (0.1 ml)] in dry THF (0.5 ml) under N_2 was added a THF solution of the α-acetoxydihydrochalcone (**14**) (100 mg in 0.5 ml) and the mixture was stirred at room temperature (4 h) before being quenched with saturated aq. NH_4Cl (5 ml) and the organic products were extracted with diethyl ether (3 × 3 ml). The extracts were washed with water (2 ml), dried (Na_2SO_4), and the solvent was removed by evaporation. PLC (hexane–benzene–acetone, 5:4:1) gave two major products, R_F 0.2 (6 mg) and 0.1 (33 mg).

The minor product (R_F 0.2), obtained as a light yellow oil (6 mg, 8%), was identified as 3-[2,4-*bis(methoxymethoxy)phenyl*]-4-(4-*methoxymethoxybenzyl*)*but-2-en*-4-*olide* (**15**) (Found: M^+, 430.1625. $C_{23}H_{26}O_8$ requires *M*, 430.1620); ^1H NMR data (Table); $\nu_{max}(CCl_4)$ 1 752 (C=O), 1 610, and 1 517 cm^{-1}.

The second compound (R_F 0.1) was identified as the dihydrotetronic acid 3-[2,4-*bis(methoxymethoxy)phenyl*]-4-(4-*methoxymethoxybenzyl*)*dihydrotetronic acid* (**16**) and was obtained as a *yellow solid* (33 mg, 41%); (Found: M^+, 448.1628. $C_{23}H_{28}O_9$ requires *M*, 448.1620); ^1H NMR data (Table); $\nu_{max}(CCl_4)$ 1 782 (C=O), 1 720, 1 619, 1 590, and 1 508 cm^{-1}.

3-(2,4-*Dihydroxyphenyl*)-4-(4-*hydroxybenzyl*)*but-2-en*-4-*olide* (**3**).—3M-HCl (1 ml) was added to a methanolic solution of the dihydrotetronic acid (**16**) (30 mg in 4 ml) and the mixture was refluxed for 20 min. Water (20 ml) was added and the product was extracted with ethyl acetate (3 × 20 ml). The combined extract was shaken successively with saturated aq. $NaHCO_3$ (10 ml) and water (10 ml), and dried over Na_2SO_4. PLC (benzene–acetone–methanol, 80:19:1) gave the *but-2-en*-4-*olide* (**3**) (R_F 0.1 as a white solid (17 mg, 85%) (Found: M^+, 298.0829. $C_{17}H_{14}O_5$ requires *M*, 198.0837); ^1H NMR data (Table); ν_{max}(KBr) 1 691 (C=O), 1 600, 1 520, and 1 305 cm^{-1}.

Acid-catalysed Hydrolysis of the Butenolide (**15**).—To a solution of the but-2-en-4-olide (**15**) (4 mg) in methanol (2 ml) was added 3M-HCl (0.5 ml) and the mixture was refluxed for 20 min. Work-up as described for the dihydrotetronic acid (**16**) gave the free phenolic butenolide (**3**) (2 mg), identical with that obtained in the previous reaction.

4-(4-*Acetoxybenzyl*)-3-(2,4-*diacetoxyphenyl*)*but-2-en*-4-*olide* (**4**).—Acetylation of the butenolide (**3**) obtained from hydrolysis of compound (**15**) and dehydration–hydrolysis of compound (**16**) gave a triacetate identical with the natural product derivative (**4**).

Acknowledgements

Support by the Foundation for Research Development, CSIR, Pretoria and by the Sentrale Navorsingsfonds of this University is acknowledged.

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Paper 0/01450H
Received 2nd *April* 1990
Accepted 17th *April* 1990