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FLAVONOIDS FROM *TEPHROSIA*—VIII[1]

THE STRUCTURE OF ELONGATIN, AN ISOFLAVONE FROM *TEPHROSIA ELONGATA* E. MEY.

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Abstract—The structure of elongatin, an isoflavone isolated from *Tephrosia elongata* E. Mey., has been established as 4',5-dihydroxy-2',5'-dimethoxy-2",2"-dimethylpyrano[5",6"-g]isoflavone.

Previous[1] studies of various *Tephrosia* species of the family Leguminosae have provided a number of novel flavonoids. In cognizance of these results we have undertaken the chemical investigation of *Tephrosia elongata*.

We now wish to report the isolation of an isoflavone, elongatin from the roots and aerial parts of *T. elongata*. Elongatin analyzed for $C_{22}H_{20}O_7$ and is assigned the structure (1) (4',5 - dihydroxy - 2',5' - dimethoxy - 2",2" - dimethylpyrano[5",6" - g]isoflavone) on the basis of chemical and spectroscopic evidence.

The IR spectrum showed strong OH absorption at 3470 cm^{-1}. The presence of one or more phenolic OH groups was indicated by the strong coloration with ethanolic ferric chloride. The band at 1660 cm^{-1} was assigned to the γ-pyrone CO group.

The nature of the groups present in elongatin was indicated by its NMR spectrum (Table 1). The singlet at τ 2·15(1H) is characteristic of the C_2 proton of an isoflavone.[2] The presence of two OMe groups was inferred from the singlets at τ 6·13(3H) and τ 6·29(3H). The latter signal is assigned to the C_2-OMe group.[3] The singlet at τ8·52(6H), the doublet at τ 4·29(1H, $J_{3',4'}$ = 10·0 Hz) and the double doublet at τ 3·25 (1H, $J_{3',4'}$ = 10·0 Hz, $J_{4',8}$ = 0·5 Hz) are assigned to the protons of the *gem*-CMe_2 group and *cis* double bond of a 2,2-dimethylchromene moiety.[4,5] The small splitting of each peak of the doublet at τ3·25 is due to the long range inter-ring coupling between the $C_{4'}$ proton and the aromatic proton at C_8 (τ3·65, $J_{4',8}$ = 0·5 Hz).[6,7] The singlets at τ3·08(1H) and τ3·33(1H) are ascribed to the *para* oriented protons at $C_{6'}$ and $C_{3'}$, respectively. The singlets at τ-3·27(1H) and τ4·15(1H), which both disappear on addition of D_2O, are assigned to two phenolic protons.

Chemical evidence for the presence of two phenolic OH groups in elongatin (1) was provided by acetylation to give the diacetate derivative (2) (ν_{max} 1770 cm^{-1}). The presence of a chelated C_5–OH, evident from the low field position (τ-3·27) of the phenolic proton resonance, was confirmed by the reaction of elongatin (1) with diazomethane to yield the 4'-O-methyl ether (3). Methylation of elongatin with MeI gave the dimethyl derivative (4).

Hydrogenation of elongatin (1) over Pd/C gave dihydroelongatin (5). The NMR spectrum shows the methylene protons of the 2,2-dimethylchroman moiety as a pair of triplets ($J_{3',4'}$ = 7·0 Hz) at τ7·26 (2H, C_4–H) and τ8·15 (2H, C_3–H).

The isoflavone structure of elongatin (1) was confirmed by mild alkaline hydrolysis of 4',5-O,O-diethylelongatin (6) to give the deoxybenzoin (7). The IR spectrum indicated the presence of a chelated CO (ν_{max} 1620 cm^{-1}). The NMR spectrum shows a two-proton singlet at τ5·64 due to the protons of the newly-formed benzylic methylene group. The intramolecular H-bonded phenolic proton appears at τ-3·06. 4',5-O,O-Diethylelongatin (6) was smoothly reformed on treatment of 7 with ethyl orthoformate.[4]

The above reactions established that elongatin is an isoflavone with a 2,2-dimethyl-2*H*-pyran residue. The alkaline hydrolysis of elongatin, even under fairly mild conditions, led to a complex mixture of products. This result is in agreement with the known lability of 2,2-dimethylchromenes to alkali if they bear OH substituents at C_5 or C_7[8]. This instability of elongatin to alkali suggested that the 2,2-dimethyl-2*H*-pyran moiety was more likely to be associated with the A-ring, as mundulone,[9] an isoflavone with a 2,2-dimethyl-2N-pyran residue on ring B, is smoothly hydrolysed to the corresponding deoxybenzoin. The mass spectrum of elongatin confirmed the above hypothesis as the fragment at *m/e* 203 (12%) could only be rationalized in terms of the structure (8).

The substitution pattern of the A-ring of elongatin was determined from NMR data. The presence of a chelated C_5-OH was evident from the low field position (τ-3·27) of one of the phenolic protons of elongatin. It has been shown[7] that acetylation of 5 - hydroxy - 2,2 - dimethylchromenes causes a marked upfield shift (*ca.* 0·30 ppm) of the C_4-H signal while the C_3-H signal suffers a small downfield shift (*ca.* 0·10 ppm). Acetylation of 4'-O-methylelongatin (3) gave the acetate derivative (9) (ν_{max} 1760 cm^{-1}). The NMR spectrum of 9 shows the C_4–H signal at τ3·54(d), an upfield shift of 0·24 ppm compared with that in 3 (τ3·30, d). The C_3–H suffered a small downfield shift (0·15 ppm). The downfield shift (0·40 ppm) of the aromatic proton signal in 3 (τ3·70, d, J = 0·5 Hz) upon acetylation of the C_5-OH locates this proton at C_8[10,11] and provides additional evidence for the substitution pattern of the A-ring of elongatin as shown in 1.

The substitution pattern of the B-ring of elongatin was established by the following procedure. Alkaline H_2O_2 oxidation of 4',5-O,O-diethyl-elongatin (6) yielded an aromatic acid, $C_{11}H_{14}O_5$. The two singlets at τ5·97(3H) and τ6·14(3H) in the NMR spectrum were assigned to the protons of two OMe groups. The presence of an OEt

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Table 1. Chemical shifts (τ) for the indicated protons in the NMR spectra of elongatin and derivatives

	2-H	5-OR	8-H[a]	2'-OMe	3'-H	4'-OR	5'-OMe	6'-H	*gem*-Me_2	3"-H[b]	4"-H[c]
		R=H				R=H					
1	2·15	−3·27	3·65	6·29	3·33	4·15	6·13	3·08	8·52	4·29	3·25
		R=Ac				R=Ac					
2	2·26	7·61	3·32	6·33	3·32	7·72	6·24	3·07	8·55	4·26	3·54
		R=H				R=Me					
3	2·21	−3·19	3·70	6·27	3·41	6·19	6·12	3·15	8·58	4·42	3·30
		R=Me				R=Me					
4	2·21	6·06	3·65	6·24	3·34	6·06	6·14	3·00	8·50	4·41	3·22
		R=Ac				R=Me					
9	2·28	7·60	3·30	6·29	3·42	6·21	6·13	3·19	8·55	4·27	3·54

[a] d, $J_{4',8}$ = 0·5 Hz
[b] d, $J_{3',4'}$ = 10·0 Hz
[c] dd, $J_{3',4'}$ = 10·0 Hz, $J_{4',8}$ = 0·5 Hz

group was evident from the triplet at τ8·49(3H) and the quartet at τ5·84(2H) (J = 7·0 Hz). The two singlets at τ2·40(1H) and τ3·44(1H) were ascribed to two *para* oriented aromatic protons. As the presence of a $C_{2'}$-OMe group in elongatin has already been demonstrated, two possible structures, viz. **10** and **11** can be formulated for the $C_{11}H_{14}O_5$ aromatic acid on the basis of its NMR data. The structure **10** was assigned to this acid by direct comparison with an authentic sample (Experimental).

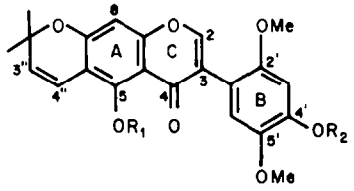
An angular fusion of the 2,2 - dimethyl - 2*H* - pyran and the A-ring in elongatin could be excluded on the basis of a direct comparison (m.p., NMR and TLC) between 4',5-O,O-dimethylelongatin (**4**) and toxicarol isoflavone methyl ether[12] (**12**) which showed the two compounds to be non-identical.

Alkaline H_2O_2 oxidation of the O-ethyl derivative of the deoxybenzoin (**7**) gave the acid (**10**) as well as the A-ring derived acid, which was characterized as the methyl ester (**13**).

With the knowledge of the structure of elongatin (**1**) at hand, it was possible to rationalize the formation of a compound obtained from its controlled alkaline peroxidation. Thus when elongatin was oxidized with H_2O_2 in alkaline medium, an intermediate oxidation product, $C_{21}H_{20}O_7$, called elongatinone (**14**) was isolated from the reaction mixture.

The most prominent differences in the NMR spectra of elongatin and elongatinone (**14**) can be summarized as follows: The signal of the C_5-OH proton in elongatin (τ-3·27) appears at τ1·96 (1H, D_2O exchangeable) in the spectrum of elongatinone. This large upfield shift of the phenolic proton signal points to a greatly reduced degree of intramolecular H-bonding between the phenolic proton and the *peri* CO group. The absence of the characteristic C_2 isoflavone proton signal (τ2·00–2·20)[2] and the appearance of the C_2-H signal at τ4·26 in the spectrum of elongatinone indicates that the observed net loss of one C atom, in the conversion of elongatin (M^+ 396) to elongatinone (**14**) (M^+ 384) occurred from the C-ring in elongatin. A possible mechanism for the formation of elongatinone is depicted in Scheme 1. The first step in the reaction sequence is envisaged as the formation of the isoflavone 2,3-epoxide.[13] The intramolecular opening of the oxirane by phenolate anion is not without precedent[14,15] and leads to the unstable bridged species **a** in Scheme 1. Re-aromatization of **a** as shown yields the coumaranone, elongatinone (**14**).

Acetylation of elongatinone with Ac_2O in pyridine yielded a compound which analyzed for $C_{27}H_{26}O_{10}$ and



(1) $R_1 = R_2 = H$

(2) $R_1 = R_2 = Ac$

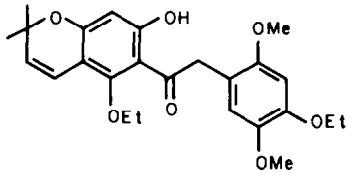
(3) $R_1 = H$, $R_2 = Me$

(4) $R_1 = R_2 = Me$

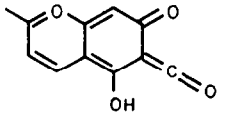
(5) $R_1 = R_2 = H$; 3",4"-dihydro

(6) $R_1 = R_2 = Et$

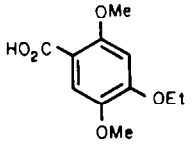
(9) $R_1 = Ac$, $R_2 = Me$



(7)



(8)



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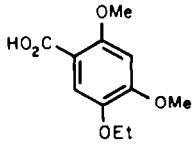
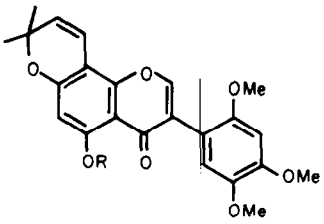
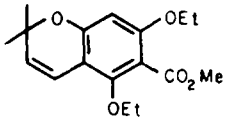


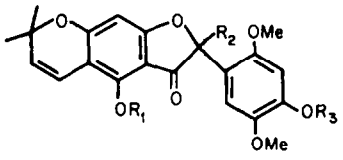
(11)



(12) R = Me



(13)



(14) $R_1 = R_2 = R_3 = H$

(15) $R_1 = R_2 = H$, $R_3 = Me$

(16) $R_1 = R_3 = Ac$, $R_2 = COCH_3$

EXPERIMENTAL

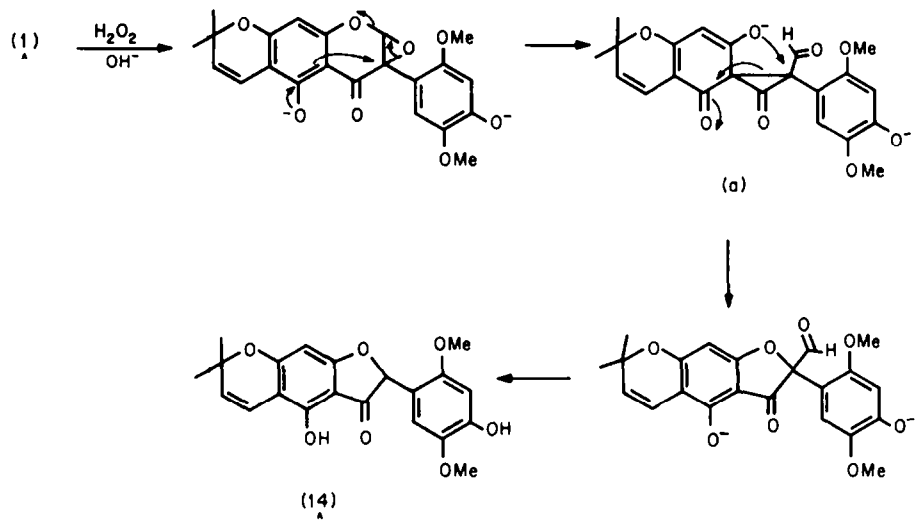
M.ps were determined with a Kofler hot-stage apparatus and are uncorrected. The IR spectra were determined on a Unicam SP-200 spectrophotometer using KBr. UV spectra refer to a soln in MeOH and were recorded on a Unicam SP-800 spectrophotometer. NMR spectra were recorded on a Varian HA-100 instrument with TMS as internal standard (τ10·00) in $CDCl_3$. Mass spectra were recorded on an AEI M.S.9 spectrometer with direct insertion technique. Silica gel (0·05–0·20 mm) was used for column chromatography.

Isolation of elongatin. The sun-dried and ground plant material (1·16 kg) was extracted with CH_2Cl_2 for 24 hr in a Soxhlet apparatus. The CH_2Cl_2 extract was concentrated to a small volume (2 l) and washed with 6N HCl. The CH_2Cl_2 was evaporated and the residue dissolved in MeOH:H_2O (9:1, 2 l). The aqueous MeOH soln was extracted with n-hexane (20 × 250 ml). Water was added to the aqueous MeOH until the ratio of MeOH to H_2O was 3:1. The resulting soln was extracted with benzene (10 × 400 ml). The combined benzene extracts yielded a brown gum (13·0 g, 1·12%). The gum was dissolved in $CHCl_3$ and fractionated by column chromatography using $CHCl_3$ as eluant. Appropriate fractions (100 ml) (TLC, $CHCl_3$:MeOH, 98:2 v/v) were combined through utilisation of the colour reaction with ethanolic $FeCl_3$ to give one main fraction.

Rechromatography of this fraction on SiO_2 with $CHCl_3$ and crystallization from MeOH gave 1 (3·5 g), m.p. 181–182°, λ_{max} 230 and 282 nm (log ϵ 4·09 and 4·24); ν_{max} 3470(OH) and 1660 (isoflavone CO) cm^{-1}; *m/e* 396(36), 381(100), 351(43), 323(21), 203(12). (Found: C, 66·71; H, 5·06. $C_{22}H_{20}O_7$ requires: C, 66·66; H, 5·09%).

Acetylation of elongatin. Acetylation of elongatin (100 mg) with Ac_2O (3 ml) and pyridine (0·5 ml) gave the diacetate 2 (95 mg), m.p. 226–227° (MeOH), λ_{max} 228, 263 and 293 nm (log ϵ 4·39, 4·52 and 4·17); ν_{max} 1770 (acetate CO) and 1650 (CO) cm^{-1}. (Found: C, 64·76; H, 4·96. $C_{26}H_{24}O_9$ requires: C, 64·91; H, 5·04%).

Methylation of elongatin. (i) A soln of elongatin (200 mg) in MeOH-ether was treated with an excess of ethereal diazomethane



Scheme 1. Proposed mechanism for the alkaline H_2O_2 oxidation of elongatin 1 to elongatinone 14.

which was assigned structure 16 on the basis of its mass, IR and NMR spectra (Experimental). The NMR spectrum of 16 showed that acetylation of the C_4-OH in elongatinone resulted in an upfield of the C_4-H signal (0·25 ppm) and a smaller downfield shift of the C_3-H signal (0·13 ppm). These shifts confirmed the substitution pattern of the A-ring of elongatinone as shown in 14.[7]

When 4′-O-methylelongatin (3) was oxidized with alkaline H_2O_2, the intermediate oxidation product, 4′-O-methylelongatinone (15) was obtained.

to give 3 (180 mg), m.p. 158–159° (MeOH–$CHCl_3$), λ_{max} 228 and 277 nm (log ϵ 4·38 and 4·52); ν_{max} 1660(CO) cm^{-1}. (Found: C, 67·05; H, 5·40. $C_{23}H_{22}O_7$ requires: C, 67·30; H, 5·41%).

(ii) A mixture of elongatin (100 mg), anhyd K_2CO_3 (1·0 g) and MeI (3 ml) in anhyd acetone (10 ml) was refluxed for 8 hr to give 4 (95 mg), m.p. 148–150° (acetone-n-hexane), λ_{max} 230 and 297 nm (log ϵ 4·30 and 4·15); ν_{max} 1655 (CO) cm^{-1}. (Found: C, 68·03; H, 5·75. $C_{24}H_{24}O_7$ requires: C, 67·91; H, 5·70%).

Dihydroelongatin (5). Elongatin (100 mg) in EtOH (50 ml) was hydrogenated at room temp over 5% Pd-C (20 mg). After 1 hr absorption of H_2 was completed and the product had precipitated.

This was dissolved by the addition of $CHCl_3$ (50 ml) and the soln after filtration yielded **5** (96 mg), m.p. 182–184° (MeOH), λ_{max} 213, 263 and 298 nm (log ϵ 4·60, 4·52 and 4·30); ν_{max} 3450(OH) and 1660(CO) cm^{-1}; NMR: τ8·62 (s, 6H, *gem*-Me_2), 8·15 (t, 2H, $J_{3',4'}$ = 7·0 Hz, C_3–H), 7·26 (t, 2H, $J_{3',4'}$ = 7·0 Hz, C_4–H), 6·26 (s, 3H, C_2-OMe), 6·12 (s, 3H, C_3-OMe), 4·42 (s, 1H, D_2O exchangeable, C_4-OH), 3·65 (s, 1H, C_8–H), 3·33 (s, 1H, C_3-H), 3·11 (s, 1H, C_6-H), 2·17 (s, 1H, C_2-H) and ~3·20 (s, 1H, D_2O exchangeable, C_5-OH). (Found: C, 66·16; H, 5·49. $C_{22}H_{22}O_7$ requires: C, 66·32; H, 5·57%).

Alkaline hydrolysis of 4',5-O,O-diethylelongatin (**6**)

(i). A mixture of elongatin (250 mg), anhyd K_2CO_3 (2·5 g) and EtI (10 ml) in anhyd acetone (50 ml) was refluxed for 8 hr to give **6** (265 mg), m.p. 154–155° (MeOH), λ_{max} 230, 267 and 297 nm (log ϵ 4·30, 4·51 and 4·15); ν_{max} 1650(CO) cm^{-1}; NMR: τ8·60 (t, 3H, J = 7·0 Hz, CH_2CH_3), 8·57 (t, 3H, J = 7·0 Hz, CH_2CH_3), 8·57 (s, 6H, *gem*-Me_2), 6·30 (s, 3H, C_2-OMe), 6·21 (s, 3H, C_5-OMe), 5·98 (q, 2H, J = 7·0 Hz, CH_2CH_3), 5·93 (q, 2H, J = 7·0 Hz, CH_2CH_3), 4·44 (d, 1H, $J_{3',4'}$ = 10·0 Hz, C_3–H), 3·44 (s, 2H, C_3-H and C_8-H), 3·27 (d, 1H, $J_{3',4'}$ = 10·0 Hz, C_4–H), 3·14 (s, 1H, C_6-H) and 2·29 (s, 1H, C_2-H). (Found: C, 68·91; H, 6·21. $C_{26}H_{28}O_7$ requires: C, 69·01; H, 6·24%).

(ii) A soln of **6** (100 mg) and KOH (1·5 g) in aqueous EtOH (1:4, 30 ml) was refluxed for 6 hr under N_2. The mixture was diluted with H_2O (30 ml), acidified (6N HCl) and extracted with CH_2Cl_2. The CH_2Cl_2 extracts yielded **7** (90 mg), m.p. 98–100° (benzene-n-hexane). λ_{max} 234, 263 and 293 nm (log ϵ 4·32, 4·64 and 4·23); ν_{max} 1620 (chelated CO) cm^{-1}; NMR: τ8·58 (s, 6H, *gem*-Me_2) 8·56 (m, 6H, 2 x CH_2CH_3), 6·30 (s, 3H, C_2-OMe), 6·20 (s, 3H, C_5-OMe), 6·02 (q, 2H, J = 7·0 Hz, CH_2CH_3), 5·90 (q, 2H, J = 7·0 Hz, CH_2CH_3), 5·64 (s, 2H, $COCH_2$), 4·43 (d, 1H, $J_{3,4}$ = 10·0 Hz, C_3-H), 3·82 (s, 1H, C_8-H), 3·53 (d, 1H, $J_{3,4}$ = 10·0 Hz, C_4-H), 3·44 (s, 1H, C_3-H), 3·32 (s, 1H, C_6-H) and ~3·06 (s, 1H, D_2O exchangeable, C_7-OH). (Found: C, 67·68; H, 6·84. $C_{25}H_{30}O_7$ requires: C, 67·86; H, 6·83%).

Transformation of the deoxybenzoin (**7**) *to 4',5-O,O-diethylelongatin* (**6**). The deoxybenzoin **7** (50 mg), ethyl *ortho*-formate (3 ml), pyridine (3 ml) and piperidine (0·3 ml) were heated under reflux (N_2 atmosphere) for 8 hr, cooled, and poured onto crushed ice. The aqueous soln was acidified (6N HCl) and extracted with CH_2Cl_2. Chromatography of the crude product on silica gel with $CHCl_3$ yielded **6** (40 mg) identical (mixed m.p., I.R. and NMR spectra) with an authentic specimen.

Acetylation of 4'-O-methylelongatin (**3**). Acetylation of **3** (50 mg) with Ac_2O (2·0 ml) and pyridine (0·5 ml) gave the acetate **9** (45 mg), m.p. 168–170° (acetone-n-hexane). λ_{max} 230, 263 and 295 nm (log ϵ 4·25, 4·40 and 4·07); ν_{max} 1760 (acetate CO) and 1650(CO) cm^{-1}. (Found: C, 66·51; H, 5·41. $C_{25}H_{24}O_8$ requires: C, 66·37; H, 5·35%).

Oxidation of 4',5-O,O-diethylelongatin (**6**) *with alkaline* H_2O_2. Diethylelongatin **6** (200 mg) was added to a 3% soln of KOH in aqueous EtOH (80% EtOH, 10 ml) and the stirred soln was warmed at 40–45° for 2 hr. During this period sufficient 30% H_2O_2 was added at 15 min intervals to maintain a gentle evolution of O_2. The resulting yellow soln was diluted with water (30 ml) and acidified (6N HCl). Extraction of this soln with CH_2Cl_2 yielded a complex mixture (TLC) of carboxylic acids. The mixture in MeOH was treated for 2 min with an excess of ethereal diazomethane to yield the methyl esters. Preparative TLC on SiO_2 afforded the main fraction which after saponification gave **10** (84 mg), m.p. 129–130° (benzene-n-hexane) (lit.,[16] m.p. 129–130°). NMR: τ8·49 (t, 3H, J = 7·0 Hz, CH_2CH_3), 6·14 (s, 3H, C_4-OMe), 5·97 (s, 3H, C_2-OMe), 5·84 (q, 2H, J = 7·0 Hz, CH_2CH_3), 3·44 (s, 1H, C_3-H) and 2·40 (s, 1H, C_6-H).

Synthesis of 2,5-dimethoxy-4-ethoxybenzoic acid (**10**). (i). A mixture of resacetophenone (5·0 g), anhyd K_2CO_3 (5 g) and EtI (5 ml) in anhyd acetone was refluxed for 3 hr to yield 4 - ethoxy - 2 - hydroxyacetophenone (5·2 g), m.p. 49–50° (EtOH) (lit.,[17] m.p. 49°).

(ii) A soln of $K_2S_2O_8$ (7·4 g) in H_2O (100 ml) was added dropwise over a period of 4 hr to a soln of 4 - ethoxy - 2 - hydroxyacetophenone (3 g) in aqueous 10% NaOH. The mixture was acidified (6N HCl, pH 6·5) after 24 hr and extracted with ether to remove unreacted material. Soxhlet liquid-liquid extraction of the aqueous soln (pH 2) with ether for 3 hr yielded 2,5 - dihydroxy - 4 - ethoxyacetophenone (3·7 g), m.p. 125–126° (EtOH). NMR: τ8·54 (t, 3H, J = 7·0 Hz), 7·48 (s, 3H, $COCH_3$), 5·62 (q, 2H, J = 7·0 Hz, CH_2CH_3), 4·8 (broad, 1H, D_2O exchangeable, C_5-OH), 3·58 (s, 1H, C_3-H), 2·80 (s, 1H, C_6-H) and ~2·50 (s, 1H, D_2O exchangeable, C_2-OH). (Found: C, 61·10; H, 6·12. $C_{10}H_{12}O_4$ requires: C, 61·22; H, 6·16%).

(iii) A mixture of 2,5 - dihydroxy - 4 - ethoxyacetophenone (1·5 g), anhyd. K_2CO_3 and MeI (8 ml) in anhyd acetone (50 ml) was refluxed for 8 hr to give the dimethyl ether (1·45 g), m.p. 125–126° (EtOH). NMR: τ8·51 (t, 3H, J = 7·0 Hz, CH_2CH_3), 7·42 (s, 3H, $COCH_3$), 6·20 (s, 3H, C_5-OMe), 6·11 (s, 3H, C_2-OMe), 5·84 (q, 2H, J = 7·0 Hz, CH_2CH_3), 3·48 (s, 1H, C_3-H) and 2·56 (s, 1H, C_6-H). (Found: C, 64·21; H, 7·12. $C_{12}H_{16}O_4$ requires: C, 64·27; H, 7·19%).

(iv) A soln of 2,5 - dimethoxy - 4 - ethoxyacetophenone (500 mg) in a mixture of dioxane (10 ml) and aqueous NaOH (10%, 10 ml) was treated with an excess of KI–I_2 reagent. The CHI_3 was filtered off and the filtrate was acidified (6N HCl). The aqueous soln was extracted with CH_2Cl_2. The CH_2Cl_2 was extracted with $NaHCO_3$ soln to yield, after work-up **10** (320 mg), m.p. 129–130° (benzene-n-hexane) (lit.,[16] m.p. 129°–130°).

6 - *Carbomethoxy* - 5,7 - *diethoxy* - 2,2 - *dimethylchroman* (**13**)

The deoxybenzoin **7** (150 mg) was ethylated with EtI by the procedure as described for elongatin (see above). The ethyl ether of **7** was oxidized with alkaline H_2O_2 by the standard procedure (see above) to yield a mixture of acids. The mixture in MeOH was esterified with an excess of ethereal diazomethane. The mixture of methyl esters was separated by preparative TLC on SiO_2 to yield **10** (38 mg) (after saponification) and the title ester **13** (30 mg) as a colourless oil. λ_{max} 224 and 285 nm; ν_{max} 1710 (ester CO) cm^{-1}; NMR: τ8·69 and 8·67 (each: t, 3H, J = 7·0 Hz, CH_2CH_3), 8·62 (s, 6H, *gem*-Me_2), 6·16 (s, 3H, CO_2Me), 6·06 and 6·02 (each: q, 2H, J = 7·0 Hz, CH_2CH_3), 4·52 (d, 1H, $J_{3,4}$ = 10·0 Hz, C_3-H), 3·85 (d, 1H, $J_{4,8}$ = 0·5 Hz, C_8-H) and 3·56 (dd, 1H, $J_{3,4}$ = 10·0 Hz, $J_{4,8}$ = 0·5 Hz, C_4-H). (Found: M^+, 306·1463. $C_{17}H_{22}O_5$ requires: M, 306·1467).

Oxidation of (*i*) *elongatin and* (*ii*) *4'-O-methylelongatin* (**3**) *with alkaline* H_2O_2

(i) Hydrogen peroxide (30%, 1·0 ml) and a soln of KOH (300 mg) in aqueous EtOH (80% EtOH, 2 ml) were added to a soln of elongatin (100 mg) in aq EtOH (80% EtOH, 8 ml) kept at 40°. After 5 min the mixture was diluted with H_2O (20 ml), acidified (6N HCl) and extracted with CH_2Cl_2 to yield **14** (66 mg), m.p. 136–137° (MeOH); λ_{max} 267 and 292 nm (log ϵ 4·65 and 4·36); $\nu_{max}^{CHCl_3}$ 3530 (OH), 3420 (OH), 1675 and 1640 cm^{-1}; NMR: τ8·52 (s, 6H, *gem*-Me_2), 6·29 (s, 3H, C_2-OMe), 6·22 (s, 3H, C_5-OMe), 4·47 (d, 1H, $J_{3',4'}$ = 10·0 Hz, C_3–H), 4·26 (s, 1H, C_2-H), 4·15 (broad, 1H, D_2O exchangeable, C_4-OH), 3·94 (broadened s, 1H, C_7-H), 3·42 (s, 1H, C_3-H), 3·40 (broadened d, 1H, $J_{3',4'}$ = 10·0 Hz, C_4–H), 3·38 (s, 1H, C_6-H) and 1·96 (broad, 1H, D_2O exchangeable, C_4-OH). (Found: C, 65·76; H, 5·11. $C_{21}H_{20}O_7$ requires: C, 65·62; H, 5·24%).

(ii) Oxidation of **3** (100 mg) by the same procedure gave **15** (78 mg), m.p. 145–146° (MeOH); ν_{max} 1660 (CO) cm^{-1}; NMR: τ8·64 (s, 6H, *gem*-Me_2); 6·35, 6·32 and 6·23 (each: s, 3H; C_2-, C_4- and C_5-OMe), 4·58 (d, 1H, $J_{3',4'}$ = 10·0 Hz, C_3–H), 4·36 (s, 1H, C_2-H), 3·96 (broadened s, 1H, C_7-H), 3·55 (s, 1H, C_3-H), 3·50 (broadened d, 1H, $J_{3',4'}$ = 10·0 Hz, C_4–H) and 3·44 (s, 1H, C_6-H). (Found: C, 66·26; H, 5·44. $C_{22}H_{22}O_7$ requires: C, 66·32; H, 5·57%).

Acetylation of elongatinone (**14**). Acetylation of **14** (30 mg) in Ac_2O (2 ml) and pyridine (1 ml) at room temp for 2 hr gave **16** (28 mg) as a colourless glass; λ_{max} 228, 254, 293 and 338 nm (log ϵ 4·43, 4·50, 3·99 and 4·32); $\nu_{max}^{CHCl_3}$ 1765 (acetate CO), 1720 (CO) and 1640 (CO) cm^{-1}; NMR: τ8·55 (s, 6H, *gem*-Me_2), 7·73 (s, 3H, C_2-$COCH_3$), 7·67 (s, 6H, C_4- and C_4'-OAc), 6·26 (s, 3H, C_2-OMe), 6·17 (s, 3H, C_5-OMe), 4·34 (d, 1H, $J_{3',4'}$ = 10·0 Hz, C_3–H), 3·65 (broadened d, 1H, $J_{3',4'}$ = 10·0 Hz, C_4–H), 3·30 (s, 1H, C_3-H), 3·18 (broadened s, 1H, C_7-H) and 2·80 (s, 1H, C_6-H). (Found: M^+, 510·1519. $C_{27}H_{26}O_{10}$ requires: M, 510·1523).

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