Total Synthesis of Sophorapterocarpan A, Maackiain, and Anhydropisatin: Application of a 1,3-Michael-Claisen Annulation to Aromatic Synthesis

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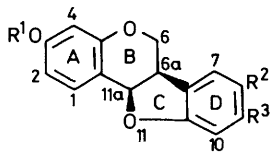
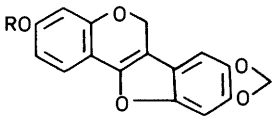
A new synthetic route to the pterocarpans using a [3C + 3C] annulation is described. 1,3-Michael-Claisen condensation of α-methylene-γ-butyrolactones with α-sulphur-substituted ketones gives 6-membered rings which have been converted into the pterocarpan framework by aromatization. Sophorapterocarpan A, maackiain, and anhydropisatin have been prepared employing this new aromatic synthesis.

In a previous paper,[1] we reported an effective synthesis of benzene-1,2,4-triols using a 1,3-Michael-Claisen condensation (a [3C + 3C] annulation). The condensation produced 6-membered rings, which were converted into aromatic nuclei bearing hydroxy and alkyl groups. We attempted to apply this method to a synthesis of the pterocarpans,[2] sophorapterocarpan A (**1**), maackiain (**2**), and anhydropisatin (**8**), in order to show the utility of the new aromatic synthesis. These pterocarpans consist of 4 rings A—D, and attention is focused on the latter in this synthesis. By choosing suitable precursor compounds, various pterocarpans can be prepared which are appropriately substituted on the D-ring. A 1,3-Michael-Claisen condensation was applied successfully to this D-ring formation and in this paper we described the synthesis of the three pterocarpans, (**1**), (**2**), and (**8**).[3]



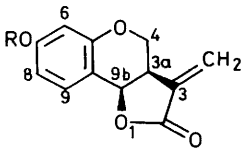


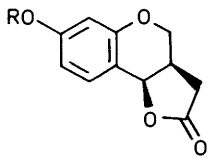
(**8**) R = Me
(**9**) R = CH_2Ph

(**1**) R^1 = H, R^2 = $CH_2CH{=}CMe_2$, R^3 = OH
(**2**) R^1 = H, R^2 = R^3 = OCH_2O
(**3**) R^1 = CH_2Ph, R^2 = $CH_2CH{=}CMe_2$, R^3 = OH
(**4**) R^1 = CH_2Ph, R^2 = $CH_2CH{=}CMe_2$, R^3 = OAc
(**5**) R^1 = H, R^2 = $CH_2CH{=}CMe_2$, R^3 = OAc
(**6**) R^1 = CH_2Ph, R^2 = R^3 = OH
(**7**) R^1 = Me, R^2 = R^3 = OH

Results and Discussion

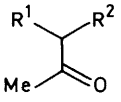
The aromatic pterocarpan D-rings were constructed from the condensation of two kinds of three-carbon (3C) unit. Four 3C units, the two methylenelactones (**10**) and (**11**) and the two ketones (**14**) and (**15**), were synthesized. Combination of these methylenelactones and ketones gave the pterocarpan skeletons, which were transformed into sophorapterocarpan A (**1**), maackiain (**2**), and anhydropisatin (**8**), respectively.





(**10**) R = CH_2Ph
(**11**) R = Me

(**12**) R = CH_2Ph
(**13**) R = Me

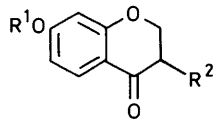


(**14**) R^1 = PhSO, R^2 = $CH_2CH{=}CMe_2$
(**15**) R^1 = R^2 = SEt
(**16**) R^1 = H, R^2 = SPh
(**17**) R^1 = SPh, R^2 = $CH_2CH{=}CMe_2$

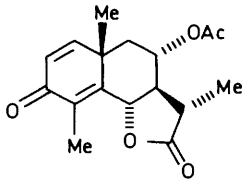
$BrCH_2CH{=}CMe_2$

(**18**)

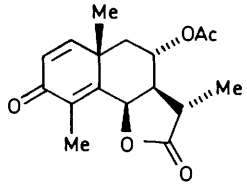
Synthesis of the 3C Units.—The methylenelactone (**10**) was prepared from 2,3-dihydro-7-hydroxy-4*H*-1-benzopyran-4-one (**19**).[4] Bromination[5] of the ketone (**19**) with $CuBr_2$ gave 3-bromo-2,3-dihydro-7-hydroxy-4*H*-1-benzopyran-4-one (**20**), which was then treated with an excess of $NaCH(CO_2Et)_2$ in tetrahydrofuran (THF) to afford diethyl (3,4-dihydro-7-hydroxy-4-oxo-2*H*-1-benzopyran-3-yl)malonate (**21**) in 41% yield from the ketone (**19**). Hydrolysis of the ketone (**21**) in acidic conditions yielded (3,4-dihydro-7-hydroxy-4-oxo-2*H*-1-benzopyran-3-yl)acetic acid (**22**) in 65% yield. Benzylation of acid (**22**) (in order to protect the 7-hydroxy group) yielded benzyl (7-benzyloxy-3,4-dihydro-4-oxo-2*H*-1-benzopyran-3-yl)acetate (**23**) (55%). Hydrolysis of the ester (**23**) under alkaline conditions gave (7-benzyloxy-3,4-dihydro-4-oxo-2*H*-1-benzopyran-3-yl)acetic acid (**24**) in 73% yield. Conversion of the acid (**24**) into *cis*-7-benzyloxy-3a,9b-dihydro-4*H*-furo[3,2-*c*][1]benzopyran-2(3*H*)-one (**12**) was accomplished by Meerwein-Ponndorf reduction in 73% yield. Its *cis*-lactone structure was established by comparison of the ^1H n.m.r. spectrum with related compounds as follows. The vicinal coupling constant of 9b-H, $J_{9b,3a}$ = 6Hz, was observed by inspection of the spectrum of compound (**12**). The vicinal coupling constants of the corresponding protons (6-H, $J_{6,7}$) of artemisin acetate (**25**) (*trans*-lactone) and 6-*epi*-artemisin acetate (**26**) (*cis*-lactone) are 11.6 Hz and 5.7 Hz, respectively.[6] The methylene lactone (**10**) was obtained in 57% yield by treatment of the ketone (**12**) with NaH and HCO_2Et in THF followed by paraformaldehyde and hexamethylphosphoric triamide (HMPA).[7] The coupling con-



(19) $R^1 = R^2 = H$
(20) $R^1 = H, R^2 = Br$
(21) $R^1 = H, R^2 = CH(CO_2Et)_2$
(22) $R^1 = H, R^2 = CH_2CO_2H$
(23) $R^1 = CH_2Ph, R^2 = CH_2CO_2CH_2Ph$
(24) $R^1 = CH_2Ph, R^2 = CH_2CO_2H$



(25)



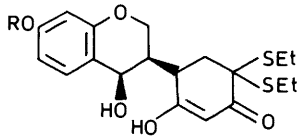
(26)

stant of 9b-H, $J_{9b,3a}$ = 6 Hz, could still be observed. *cis*-3a,9b-Dihydro-7-methoxy-3-methylene-4*H*-furo[3,2-*c*][1]benzopyran-2(3*H*)-one (**11**) was obtained from *cis*-3a,9b-dihydro-7-methoxy-4*H*-furo[3,2-*c*][1]benzopyran-2(3*H*)-one (**13**)[8] in the same way in 60% yield. The vicinal coupling constant of 9b-H, $J_{9b,3a}$ = 6 Hz, could be observed in the ^{1}H n.m.r. spectrum.

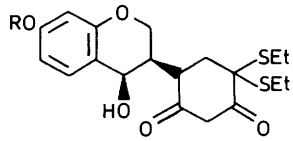
2-Methyl-5-phenylsulphinylhept-2-en-6-one (**14**) was derived from 1-(phenylthio)propan-2-one (**16**)[9] as follows. Treatment of the ketone (**16**) with NaH in DMF followed by 1-bromo-3-methylbut-2-ene (**18**) furnished 2,7-dimethyl-5-phenylthiohept-2-en-6-one (**17**) in 79% yield. Oxidation of ketone (**17**) with *m*-chloroperbenzoic acid (MCPBA) gave the ketone (**14**) in 60% yield. 1,1-Bis(ethylthio)propan-2-one (**15**) was prepared according to the literature procedure.[10]

Condensation of the 3C *Units.*—Sophorapterocarpan A (**1**) was derived from the condensation of *cis*-7-benzyloxy-3a,9b-dihydro-3-methylene-4*H*-furo[3,2-*c*][1]benzopyran-2(3*H*)-one (**10**) with ketone (**14**). The former possesses the A, B, and C ring components, and part of the D ring component. The latter has a 3C unit of the D-ring and a 3-methylbut-2-enyl group which was expected to form the side chain of (**1**). The annulation was performed in the presence of NaH in 1,2-dimethoxyethane (DME). Thermolysis of the annulated compound in acetic acid gave the pterocarpan framework, *cis*-3-benzyloxy-6a,11a-dihydro-8-(3-methylbut-2-enyl)-6*H*-benzofuro[3,2-*c*][1]benzopyran-9-ol (**3**), in 25% overall yield from the lactone (**10**). The formation of the D-ring was confirmed by the appearance of simple aromatic proton signals at δ 6.94 (1 H, s, 7-H) and δ 6.35 (1 H, s, 10-H) in the ^{1}H n.m.r. spectrum of compound (**3**). The vicinal coupling constant of 11a-H, $J_{11a,6a}$ = 6.7 Hz, confirms the *cis* structure of compound (**3**). Acetylation of the alcohol (**3**) (to prevent cyclization of the side chain in the following step) gave the acetate (**4**) in 84% yield. The benzyl group of acetate (**4**) was removed with BCl_3 in CH_2Cl_2 at −50 °C to give the monoacetate (**5**) in 68% yield.[11] Hydrolysis of the monoacetate (**5**) under alkaline conditions afforded (±)-sophorapterocarpan A (**1**) in 65% yield. The synthetic product (**1**) was confirmed to be the authentic sophorapterocarpan A by a comparison of their i.r., ^{1}H n.m.r., and u.v. spectra, and behaviour on t.l.c. with benzene–AcOEt (1:1) as eluant.[12]

Maackiain contains an aromatic D-ring with a 1,2,4-benzenetrioxy skeleton. This ring was constructed from the lactone (**10**) and 1,1-bis(ethylthio)propan-2-one (**15**). The latter was expected to be incorporated into the 1,2-dioxy system on the aromatic ring. The annulation using the lactone (**10**) and the ketone (**15**) was carried out with NaH in DME in the same way as described above to give two acidic carbonyl compounds which were separated by column chromatography. Compound



(27) R = CH_2Ph
(28) R = Me



(29) R = CH_2Ph
(30) R = Me

(**27**) in the earlier fraction was found to have an enol structure from the following spectral data. It showed a carbonyl absorption at 1 620 cm^{-1} in the i.r. spectrum and olefinic proton signals at δ 5.33 (1 H, d, *J* 1 Hz, 5-H) in its ^{1}H n.m.r. spectrum. Compound (**29**) in the next fraction existed in the keto form. It showed a carbonyl absorption at 1 716 cm^{-1} in the i.r. spectrum and proton signals at δ 2.97 and 3.19 (each 1 H, d, *J* 14.5 Hz, 5-H_2). Structures (**27**) and (**29**) were determined from these spectral data and the results which follow for the transformation to the pterocarpan structure. Dethioketalization of compound (**27**) with mercury(II) perchlorate trihydrate [$Hg(ClO_4)_2 \cdot 3H_2O$ (MPC)][13] followed by acidic treatment gave *cis*-3-benzoyloxy-6a,11a-dihydro-6*H*-benzofuro[3,2-*c*][1]benzopyran-8,9-diol (**6**) in 44% yield. Two aromatic proton signals at δ 6.77 (1 H, s, 7-H) and 6.42 (1 H, s, 10-H) in the n.m.r. spectrum of compound (**6**) confirm formation of the D-ring. Its *cis* structure was established from the vicinal coupling constant of 11a-H ($J_{11a,6a}$ = 6.7 Hz). Similar treatment of compound (**29**) afforded compound (**6**) in 52% yield. When this was heated with CsF and CH_2Br_2 in DMF, 3-benzyloxy-6*H*-[1,3]dioxolo[5,6]benzofuro[3,2-*c*][1]benzopyran (**9**) was formed in 63% yield.[14] This unexpected dehydrogenation was accompanied by the methylenation of compound (**6**); the dehydrogenation mechanism is unknown. As compound (**9**) has already been converted into maackiain (**2**) by a reductive procedure,[15] the synthesis of compound (**9**) constitutes a formal synthesis of the pterocarpan (**2**).

The dehydrogenation reaction which took place during the methylenation of compound (**6**) was applied to the synthesis of anhydropisatin. The condensation of *cis*-3a,9b-dihydro-7-methoxy-3-methylene-4*H*-furo[3,2-*c*][1]benzopyran-2(3*H*)-one (**11**) with the ketone (**15**) was carried out in the same way as for the lactone (**10**). Annulation gave two isomers, (**28**) [40% from (**11**)] and (**30**) [8% from (**11**)], which were separated by column chromatography. Compound (**28**) showed a carbonyl absorption at 1 625 cm^{-1} in the i.r. spectrum and an olefinic proton signal at δ 5.33 (1 H, d, *J* 1 Hz, 5-H) in its ^{1}H n.m.r. spectrum. Compound (**30**) showed a carbonyl absorption at 1 708 cm^{-1} and proton signals at δ 2.96 and 3.08 (each 1 H, d, *J* 14.5 Hz, 5-H_2). These spectral features are similar to those of compounds (**27**) and (**29**). Compound (**28**) afforded *cis*-6a,11a-dihydro-3-methoxy-6*H*-benzofuro[3,2-*c*][1]benzopyran-8,9-diol (**7**) in 51% yield on treatment with MPC followed by AcOH. The formation of the aromatic D-ring was confirmed by the existence of simple aromatic proton signals at δ 6.77 (1 H, s, 7-H) and 6.24 (1 H, s, 10-H) in its ^{1}H n.m.r. spectrum. The vicinal coupling constant of 11a-H ($J_{11a,6a}$ = 6.7 Hz) suggests a *cis* structure. Compound (**30**) gave the diol (**7**) in 55% yield in the same way. 3-Methoxy-6*H*-[1,3]dioxolo[5,6]benzofuro[3,2-*c*]-[1]benzopyran (**8**) was derived from the diol (**7**) by a methylenation (accompanying the dehydrogenation) under the same conditions noted above. Compound (**8**) was shown to be identical with natural anhydropisatin by means of i.r., ^{1}H n.m.r., and u.v. spectra and mixed m.p.[16]

In conclusion, the pterocarpans, sophorapterocarpan A, maackiain, and anhydropisatin, have been synthesized from α-

methylene-γ-butyrolactones and α-sulphur-substituted ketones by a 1,3-Michael-Claisen condensation. The present procedure provides a new route to pterocarpans and has potential value for the synthesis of aromatic natural products.

Experimental

I.r. spectra were recorded on a Hitachi 285 spectrophotometer or a Hitachi 270-30 spectrometer. ^{1}H N.m.r. spectra were recorded on a JEOL-JNM-PMX 60si spectrometer or a JNM-GX270 FT spectrometer using tetramethylsilane as an internal standard. U.v. spectra were recorded on a Hitachi model 200-10 spectrophotometer. M.p.s. were measured on a Yanako model MP micro melting point apparatus and are uncorrected. High-resolution mass spectra were obtained on a JEOL JMS-DX300 mass spectrometer. Sodium hydride (NaH) was suspended in mineral oil (60%). All extracts were dried over anhydrous $MgSO_4$. Column chromatography and t.l.c. were performed with Kieselgel 60 (70—230 mesh) and Kieselgel 60 PF_{254} (Merck), respectively.

Diethyl (3,4-*Dihydro*-7-*hydroxy*-4-*oxo*-2H-1-*benzopyran*-3-*yl*)*malonate* (**21**).—A mixture of 2,3-dihydro-7-hydroxy-4*H*-1-benzopyran-4-one (**19**) (20 g) and $CuBr_2$ (54.4 g) in EtOAc (300 ml) was stirred under reflux for 2.5 h. The mixture was filtered, and the filtrate was washed with saturated aqueous $NaHCO_3$, water, and brine, and then dried. Evaporation of solvent under reduced pressure gave 3-*bromo*-2,3-*dihydro*-7-*hydroxy*-4H-1-*benzopyran*-4-*one* (**20**); δ_H(60 MHz; CD_3OD–$CDCl_3$, 1:5) 4.55 (3 H, br s), 6.35 (1 H, d, *J* 2 Hz), 6.50 (1 H, dd, *J* 2 and 8 Hz), 7.73 (1 H, d, *J* 8 Hz). A solution of diethyl malonate (48.8 g) in THF (150 ml) was added to a suspension of NaH (12.2 g) in THF (200 ml) at 0 °C, and the mixture was stirred at room temperature for 15 min. To the resulting solution was added a solution of the ketone (**20**) in THF (150 ml) at room temperature and stirring was continued for 16 h. The reaction mixture was poured into water and acidified with 10% HCl. The product was extracted with Et_2O and the organic extract was washed with saturated aqueous $NaHCO_3$, water, and brine, and then dried. After evaporation of solvent, the crude product was chromatographed on silica gel with 3% (v/v) MeOH–$CHCl_3$ to give the *pure ester* (**21**) (16 g, 41%) as a pale yellow oil, $\nu_{max.}$($CHCl_3$) 3 580, 3 200, 1 730, 1 680, and 1 607 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 1.30 (6 H, t), 3.66 (1 H, m), 4.0—4.6 (7 H, m), 6.33 (1 H, d, *J* 2 Hz), 6.50 (1 H, dd, *J* 2 and 8 Hz), and 7.70 (1 H, d, *J* 8 Hz) (Found: M^+, 322.1078. $C_{16}H_{18}O_7$ requires *M*, 322.1053).

3,4-*Dihydro*-7-*hydroxy*-4-*oxo*-2H-1-*benzopyran*-3-*ylacetic Acid* (**22**).—A mixture of the ester (**21**) (16 g), AcOH (8 ml), 90% HCO_2H (42 ml), and conc. H_2SO_4 (8 drops) was refluxed for 16 h. After evaporation of the solvent under reduced pressure, the residue was dissolved in Et_2O and the acid was extracted with saturated aqueous $NaHCO_3$. This solution was washed with Et_2O and acidified with 10% HCl. The product was extracted with Et_2O and the extract was washed with brine, and then dried. After evaporation of the solvent, the residue was recrystallized from benzene to give the title compound as *colourless crystals* (7.2 g, 65%), m.p. 185—188 °C, $\nu_{max.}$(Nujol) 3 300, 3 170, 1 710br, 1 640, and 1 600 cm^{-1}; δ_H(60 MHz; CD_3OD–$CDCl_3$, 1:5) 2.42 (1 H, dd, *J* 8 and 17 Hz), 2.93 (1 H, dd, *J* 5 and 17 Hz), 3.20 (1 H, m), 4.1—4.6 (2 H, m), 6.30 (1 H, d, *J* 3 Hz), 6.55 (1 H, dd, *J* 3 and 8 Hz), and 7.70 (1 H, d, *J* 8 Hz) (Found: M^+, 222.0541. $C_{11}H_{10}O_5$ requires *M*, 222.0529).

Benzyl (7-*Benzyloxy*-3,4-*dihydro*-4-*oxo*-2H-1-*benzopyran*-3-*yl*)*acetate* (**23**).—A mixture of acid (**22**) (22.2 g), benzyl bromide (37.6 g), K_2CO_3 (40 g), acetone (300 ml), and *N*,*N*-dimethylformamide (DMF) (100 ml) was refluxed for 5 h. After filtration, the mixture was evaporated under reduced pressure and the residue poured into water. The product was extracted with Et_2O and the organic extract was washed with water and brine, and then dried. Evaporation of solvent under reduced pressure gave an oil which was subjected to column chromatography with CH_2Cl_2 as eluant to give the title compound as *colourless crystals* (22 g, 55%), m.p. 101—103 °C (EtOH) (Found: C, 74.85; H, 5.25. $C_{25}H_{22}O_5$ requires C, 74.61; H, 5.51%); $\nu_{max.}$($CHCl_3$) 1 730, 1 680, and 1 605 cm^{-1} (Found: M^+, 402.1465. $C_{25}H_{22}O_5$ requires *M*, 402.1468).

7-*Benzyloxy*-3,4-*dihydro*-4-*oxo*-2H-1-*benzopyran*-3-*ylacetic Acid* (**24**).—A mixture of the ester (**23**) (21 g), NaOH (2.09 g), MeOH (120 ml), and water (100 ml) was refluxed for 1.5 h. The reaction mixture was poured into water and washed with Et_2O. The aqueous solution was acidified with 10% HCl and the precipitate formed was filtered off, washed with water, and dried to yield the *title compound* (11.9 g, 73%), m.p. 152—154 °C (benzene), $\nu_{max.}$($CHCl_3$) 1 715, 1 680, and 1 605 cm^{-1}; δ_H(60 MHz; CD_3OD—$CDCl_3$, 1:5) 2.40 (1 H, dd, *J* 8 and 18 Hz), 2.96 (1 H, dd, *J* 5 and 18 Hz), 3.10 (1 H, m), 4.1—4.6 (2 H, m), 5.10 (2 H, s), 5.50 (1 H, d, *J* 3 Hz), 6.66 (1 H, dd, *J* 3 and 8 Hz), 7.35 (5 H, s), and 7.80 (1 H, d, *J* 8 Hz) (Found: M^+, 312.1007. $C_{18}H_{16}O_5$ requires *M*, 312.0998).

cis-7-*Benzyloxy*-3a,9b-*dihydro*-4H-*furo*[3,2-c][1]*benzopyran*-2(3H)-*one* (**12**).—A mixture of aluminium (8.65 g) and $HgCl_2$ (trace) in Bu^{s}OH (300 ml) was refluxed until the solid was dissolved. A suspension of the acid (**24**) (40 g) in Bu^{s}OH (200 ml) was added to this mixture and the solution was refluxed for 14 h. Solvent was evaporated under reduced pressure and the residue was acidified with 10% HCl and the mixture stirred for 8 h. The resulting precipitate was collected, dried, and recrystallized from EtOH to give the title compound as *colourless needles* (27.5 g, 73%), m.p. 105—108 °C (MeOH) (Found: C, 72.7; H, 5.25. $C_{18}H_{16}O_4$ requires C, 72.96; H, 5.44%); $\nu_{max.}$(Nujol) 1 780 and 1 620 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 2.2—3.1 (3 H, m, 3-H_2 and 3a-H), 3.73 (1 H, dd, *J* 8 and 11 Hz, 4-$H_{ax.}$), 4.15 (1 H, dd, *J* 4 and 11 Hz, 4-$H_{eq.}$), 5.01 (2 H, s, CH_2Ph), 5.38 (1 H, d, *J* 6 Hz, 9b-H), 6.48 (1 H, d, *J* 3 Hz, 6-H), 6.60 (1 H, dd, *J* 3 and 8 Hz, 8-H), 7.25 (1 H, d, *J* 8 Hz, 9-H), and 7.33 (5 H, s, CH_2*Ph*) (Found: M^+, 296.1038. $C_{18}H_{16}O_4$ requires *M*, 296.1049).

cis-7-*Benzyloxy*-3a,9b-*dihydro*-3-*methylene*-4H-*furo*[3,2-c]-[1]*benzopyran*-2(3H)-*one* (**10**).—A mixture of the ketone (**12**) (21 g), NaH (2.7 g), and HCO_2Et (6.3 g) in THF (190 ml) was stirred at room temperature for 16 h. To the solidified reaction mixture was added HMPA (140 ml) and paraformaldehyde (18.5 g). The mixture was stirred for 24 h at room temperature and then poured into water. The product was extracted with Et_2O and the organic extract was washed with brine, and then dried. Solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel with CH_2Cl_2 to give the title compound as *colourless crystals* (12.5 g, 57%), m.p. 117—118 °C (Et_2O) (Found: C, 74.25; H, 5.45. $C_{19}H_{16}O_4$ requires C, 74.01; H, 5.23%); $\nu_{max.}$(Nujol) 1 765 and 1 615 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 3.3—4.3 (3 H, m, 3a-H and 4-H_2), 5.00 (2 H, s, CH_2Ph), 5.33 (1 H, d, *J* 6 Hz, 9b-H), 5.75, 6.33 (each 1 H, d, *J* 1 Hz, =CH_2), 6.50 (1 H, d, *J* 3 Hz, 6-H), 6.60 (1 H, dd, *J* 3 and 8 Hz, 8-H), 7.30 (1 H, d, *J* 8 Hz, 9-H), and 7.33 (5 H, s, CH_2*Ph*) (Found: M^+, 308.1061. $C_{19}H_{16}O_4$ requires *M*, 308.1049).

2-*Methyl*-5-*phenylthiohept*-2-*en*-6-*one* (**17**).—A solution of 1-(phenylthio)propan-2-one (**16**) (6.79 g) in DMF was added to a suspension of NaH (1.6 g) in DMF (20 ml) at 0 °C with stirring. The mixture was stirred for 15 min at room temperature after which a solution of 1-bromo-3-methylbut-2-ene (**18**) (6.18

g) in DMF (10 ml) was added to it. Stirring was continued for 1 h at room temperature after which the solution was poured into water and acidified with 10% HCl. The product was extracted with Et_2O and the organic extract was washed with saturated aqueous $NaHCO_3$, water, and brine, and then dried. Solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel with benzene to give the title compound as a *colourless oil* (7.8 g, 79%), $\nu_{max.}$(film) 1 705 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 1.60 (3 H, br s, =CMe), 1.69 (3 H, br s, =CMe), 2.20 (3 H, s, COMe), 2.1—2.6 (2 H, m, CH_2), 3.62 (1 H, t, *J* 7.5 Hz, S–CH), 5.09 (1 H, br t, =CH), and 7.1—7.4 (5 H, m, SPh) (Found: M^+, 234.1065. $C_{14}H_{18}OS$ requires *M*, 234.1078).

2-*Methyl*-5-*phenylsulphinylhept*-2-*en*-6-*one* (**14**).—A solution of MCPBA (3.44 g) in CH_2Cl_2 (70 ml) was added to a solution of the ketone (**17**) (4.68 g) in CH_2Cl_2 (50 ml) at 0 °C. The mixture was stirred for 30 min at room temperature after which it was washed with saturated aqueous $NaHCO_3$ and water and then dried. Evaporation of solvent under reduced pressure at 25 °C gave an oil which was chromatographed on silica gel with 1% (v/v) MeOH–CH_2Cl_2 to give the title compound as a *colourless oil* (3 g, 60%), $\nu_{max.}$($CHCl_3$) 1 700 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 1.59 (3 H, br s, =CMe), 1.66 (3 H, br s, =CMe), 1.95 and 2.08 (each 1.5 H, s, COMe), 2.3—2.7 (2 H, m, CH_2), 3.55 (1 H, m, SCH), 4.98 (1 H, m, =CH), and 7.4—7.6 (5 H, m, Ph).

cis-3-*Benzyloxy*-6a,11a-*dihydro*-8-(3-*methylbut*-2-*enyl*)-6H-*benzofuro*[3.2-c][1]*benzopyran*-9-*ol* (**3**).—A solution of the ketone (**14**) (3 g) in DME (15 ml) was added to a suspension of NaH (0.15 g) in DME (20 ml) at 0 °C with stirring. To the reaction mixture was added a solution of compound (**10**) (2.96 g) in DME (20 ml) at 0 °C. Stirring was continued for 16 h at room temperature after which NaH (0.15 g) was added to the solution at 0 °C; it was then stirred for a further 6 h at room temperature. Solvent was evaporated under reduced pressure and water was added to the residue. The aqueous solution was washed with Et_2O and acidified with 10% HCl. The product was extracted with Et_2O and the extract washed with brine, and then dried. Solvent was evaporated under reduced pressure then benzene (40 ml) was added to the residue and the solution was refluxed for 1 h. Evaporation of solvent gave a brown residue which was subjected to column chromatography with 0.5% (v/v) MeOH–CH_2Cl_2 to give the title compound as *colourless crystals* (1.04 g, 25%), m.p. 139—141 °C (from benzene) (Found: C, 77.95; H, 6.3. $C_{27}H_{26}O_4$ requires C, 78.24; H, 6.32%); $\nu_{max.}$(KBr) 3 440, 1 620, and 1 585 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.76 (3 H, s, Me), 1.77 (3 H, s, Me), 3.28 (2 H, d, *J* 7.2 Hz, CH_2CH=), 3.48 (1 H, m, 6a-H), 3.62 (1 H, dd, *J* 10.8 and 10.8 Hz, 6-$H_{ax.}$), 4.23 (1 H, dd, *J* 4.7 and 10.8 Hz, 6-$H_{eq.}$), 5.04 (2 H, s, CH_2Ph), 5.26 (1 H, s, OH), 5.29 (1 H, br t, CH_2C*H*=), 5.45 (1 H, d, *J* 6.7 Hz, 11a-H), 6.35 (1 H, s, 10-H), 6.54 (1 H, d, *J* 2.5 Hz, 4-H), 6.70 (1 H, dd, *J* 2.5 and 8.5 Hz, 2-H), 6.94 (1 H, s, 7-H), and 7.30—7.45 (6 H, m, 1-H and CH_2*Ph*) (Found: M^+, 414.1842. $C_{27}H_{26}O_4$ requires *M*, 414.1831).

cis-9-*Acetoxy*-3-*benzyloxy*-6a,11a-*dihydro*-8-(3-*methylbut*-2-*enyl*)-6H-*benzofuro*[3,2-c][1]*benzopyran* (**4**).—A mixture of alcohol (**3**) (500 mg), Ac_2O (2 ml), and pyridine (4 ml) was allowed to stand for 16 h at room temperature. Solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel with CH_2Cl_2 to give the title compound as *colourless crystals* (462 mg, 84%), m.p. 120—122 °C (EtOH); $\nu_{max.}$(KBr) 1 755 and 1 620 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.70 (3 H, s, Me), 1.75 (3 H, s, Me), 2.28 (3 H, s, Ac), 3.15 (2 H, d, *J* 7.5 Hz, CH_2CH=), 3.54 (1 H, m, 6a-H), 3.68 (1 H, dd, *J* 10.8 and 10.8 Hz, 6-$H_{ax.}$), 4.26 (1 H, dd, *J* 4.8 and 10.8 Hz, 6-$H_{eq.}$), 5.05 (2 H, s, CH_2Ph), 5.20 (1 H, br t, CH_2C*H*=), 5.50 (1 H, d, *J* 6.7 Hz, 11a-H), 6.52 (1 H, s, 10-H), 6.54 (1 H, d, *J* 2.4 Hz, 4-H), 6.70 (1 H, dd, *J* 2.4 and 8.5 Hz, 2-H), 6.94 (1 H, s, 7-H), and 7.30—7.45 (6 H, m, 1-H and CH_2*Ph*) (Found: M^+, 456.1951. $C_{29}H_{28}O_5$ requires *M*, 456.1937).

cis-9-*Acetoxy*-6a,11a-*dihydro*-8-(3-*methylbut*-2-*enyl*)-6H-*benzofuro*[3,2-c][1]*benzopyran*-3-*ol* (**5**)—A solution of BCl_3 (40 4-mg) in CH_2Cl_2 (2 ml) was added to a solution of compound (**4**) (100 mg) in CH_2Cl_2 (3 ml) at −50 °C. The mixture was stirred for 10 min and then poured into water and extracted with CH_2Cl_2. The organic extract was washed with water, dried, and evaporated under reduced pressure. The residue was chromatographed on silica gel with 1% (v/v) MeOH–CH_2Cl_2 to give the title compound as *colourless crystals* (55 mg, 68%), m.p. 165—168 °C (EtOH) (Found: C, 72.35; H, 6.25. $C_{22}H_{22}O_5$ requires C, 72.11; H, 6.05%); $\nu_{max.}$($CHCl_3$) 3 590, 3 350, 1 755, and 1 620 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.70 (3 H, s, Me), 1.75 (3 H, s, Me), 2.29 (3 H, s, Ac), 3.15 (2 H, d, *J* 7 Hz, CH_2CH=), 3.52 (1 H, m, 6a-H), 3.60 (1 H, dd, *J* 10.5 and 10.5 Hz, 6-$H_{ax.}$), 4.21 (1 H, dd, *J* 4 and 10.5 Hz, 6-$H_{eq.}$), 5.20 (1 H, br t, CH_2C*H*=), 5.46 (1 H, d, *J* 6.3 Hz, 11a-H), 6.37 (1 H, d, *J* 2.4 Hz, 4-H), 6.51 (1 H, dd, *J* 2.4 and 8.5 Hz, 2-H), 6.52 (1 H, s, 10-H), 7.26 (1 H, s, 7-H), and 7.35 (1 H, d, *J* 8.5 Hz, 1-H) (Found: M^+, 366.1435. $C_{22}H_{22}O_5$ requires *M*, 366.1468).

cis-6a,11a-*Dihydro*-8-(3-*methylbut*-2-*enyl*)-6H-*benzofuro*-[3,2-c][1]*benzopyran*-3,9-*diol* [(±)-*sophorapterocarpan A*] (**1**).—A mixture of alcohol (**5**) (20 mg), NaOH (6 mg), MeOH (1 ml), and water (1 ml) was refluxed for 2 h. Methanol was evaporated under reduced pressure and the residue was acidified with 10% HCl. The product was extracted with Et_2O and the organic extract was washed with brine, dried, and evaporated to give crystals which were subjected to preparative thin layer chromatography [1% (v/v) MeOH—CH_2Cl_2] to afford compound (**5**) as *colourless crystals* (12.5 mg, 65%), m.p. 52.0—53.0 °C (cyclohexane), $\nu_{max.}$($CHCl_3$) 3 600, 3 350, 1 620, and 1 600 cm^{-1}; $\lambda_{max.}$(EtOH) 290 (log ε 3.95); δ_H(270 MHz; $CDCl_3$) 1.77 (6 H, s, 2 × Me), 3.28 (2 H, d, *J* 7 Hz, CH_2CH=), 3.48 (1 H, m, 6a-H), 3.61 (1 H, dd, *J* 10.8 and 10.8 Hz, 6-$H_{ax.}$), 4.23 (1 H, dd, *J* 4.7 and 10.8 Hz, 6-$H_{eq.}$), 5.08 (1 H, s, OH), 5.21 (1 H, s, OH), 5.29 (1 H, br t, CH_2C*H*=), 5.45 (1 H, d, *J* 6.5 Hz, 11a-H), 6.36 (1 H, s, 10-H), 6.40 (1 H, d, *J* 2.5 Hz, 4-H), 6.53 (1 H, dd, *J* 2.5 and 8.4 Hz, 2-H), 6.95 (1 H, s, 7-H), and 7.37 (1 H, d, *J* 8.4 Hz, 1-H) (Found: M^+, 324.1346. $C_{20}H_{20}O_4$ requires *M*, 324.1362).

cis-7-*Benzyloxy*-4-*hydroxychroman*-3-*yl*-3,3-*bis*(*ethylthio*)-6-*hydroxycyclohex*-5-*en*-4-*one* (**27**) *and* cis-7-*Benzyloxy*-4-*hydroxychroman*-3-*yl*-3,3-*bis*(*ethylthio*)*cyclohexane*-4,6-*dione* (**29**).—A solution of the ketone (**15**) (2.7 g) in DME (15 ml) was added to a suspension of NaH (0.3 g) in DME (20 ml) at 0 °C. The mixture was stirred for 15 min at room temperature and then a solution of compound (**10**) (4.7 g) in DME (20 ml) was added to the reaction mixture at 0 °C. Stirring was continued for 16 h at room temperature, and then NaH (0.3 g) was added to the solution at 0 °C and stirring was continued for a further 6 h at room temperature. After evaporation of the solvent under reduced pressure, water was added to the residue and the solution was washed with ether. The water layer was acidified with 10% HCl and extracted with CH_2Cl_2. The organic extract was washed with water and brine, and then dried. Evaporation of the solvent under reduced pressure followed by column chromatography on silica gel with 1% (v/v) MeOH–CH_2Cl_2 gave compounds (**27**) and (**29**). *Compound* (**27**) (3.15 g, 42%), m.p. 124—125 °C, $\nu_{max.}$($CHCl_3$) 3 570, 1 620, and 1 580 cm^{-1}; δ_H(60 MHz; 5% CD_3OD–$CDCl_3$) 1.15 (3 H, t, *J* 7 Hz, CH_2CH_3), 1.27 (3 H, t, *J* 7 Hz, CH_2CH_3), 2.2—2.8 (5 H, m, 2 × SCH_2 and 2-H), 3.1—3.6 (1 H, m, 1-H), 4.17 (2 H, br s, 2′-H_2), 4.99 (2 H, br s, CH_2Ph), 5.33 (1 H, d, *J* 1 Hz, 5-H), 5.72 (1 H, d, *J* 7 Hz, 4′-H), 6.44 (1 H, d, *J* 3 Hz, 8′-H), 6.60 (1 H, dd, *J* 3 and

8 Hz, 6′-H), 7.19 (1 H, d, *J* 8 Hz, 5′-H), and 7.26 (5 H, s, CH_2Ph) (Found: M^+, 486.1510. $C_{26}H_{30}O_5S_2$ requires *M*, 486.1535). *Compound* (**29**) (1.46 g, 20%), m.p. 147—149 °C, $\nu_{max.}$(Nujol) 3 600, 1 716, 1 622, and 1 590 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7.5 Hz, CH_2CH_3), 1.25 (3 H, t, *J* 7.5 Hz, CH_2CH_3), 2.16 (1 H, dd, *J* 12.5 and 14.7 Hz, 2-H), 2.37 (1 H, dd, *J* 5.2 and 14.7 Hz, 2-H), 2.5—2.7 (4 H, m, 2 × SCH_2), 2.97 (1 H, d, *J* 14.5 Hz, 5-H), 3.09 (1 H, m, 1-H), 3.19 (1 H, d, *J* 14.5 Hz, 5-H), 3.93 (1 H, dd, *J* 10 and 11.3 Hz, 2′-$H_{ax.}$), 4.15 (1 H, dd, *J* 4.6 and 11.3 Hz, 2′-$H_{eq.}$), 4.80 (1 H, br s, OH), 5.01 (2 H, s, CH_2Ph), 5.03 (1 H, d, *J* 6 Hz, 4′-H), 6.50 (1 H, d, *J* 2.5 Hz, 8′-H), 6.63 (1 H, dd, *J* 2.5 and 8 Hz, 6′-H), 7.24 (1 H, d, *J* 8 Hz, 5′-H), and 7.39 (5 H, br s, CH_2Ph) (Found: M^+, 486.1514. $C_{26}H_{30}O_5S_2$ requires *M*, 486.1535).

cis-3-*Benzyloxy*-6a,11a-*dihydro*-6H-*benzofuro*[3,2-c][1]*benzopyran*-8,9-*diol* (**6**).—A solution of MPC (900 mg) in THF (6 ml) was added to a solution of compound (**27**) (486 mg) in THF (5 ml) and $CHCl_3$ (10 ml) with stirring at room temperature. Stirring was continued for 15 min and the precipitates formed were filtered off. Water was added to the filtrate and the water layer was extracted with CH_2Cl_2. The organic extract was washed with water, dried, and then evaporated under reduced pressure. To the resulting residue was added AcOH (8 ml) and the solution was refluxed for 1 h. Solvent was evaporated under reduced pressure and the residue was subjected to column chromatography with 2% (v/v) MeOH–CH_2Cl_2 to yield compound (**6**) as *pale yellow crystals* (160 mg, 44%), m.p. 163—164 °C (benzene) (Found: C, 72.68; H, 5.23. $C_{22}H_{18}O_5$ requires C, 72.92; H, 5.01%); $\nu_{max.}$(KBr) 3 316, 1 622, and 1 588 cm^{-1}; δ_H(270 MHz; 5% CD_3OD–$CDCl_3$) 3.45 (1 H, m, 6a-H), 3.60 (1 H, dd, *J* 11 and 11 Hz, 6-$H_{ax.}$), 4.22 (1 H, dd, *J* 4.7 and 11 Hz, 6-$H_{eq.}$), 5.05 (2 H, s, CH_2Ph), 5.42 (1 H, d, *J* 6.7 Hz, 11a-H), 6.42 (1 H, s, 10-H), 6.54 (1 H, d, *J* 2.4 Hz, 4-H), 6.70 (1 H, dd, *J* 2.4 and 8.6 Hz, 2-H), 6.77 (1 H, s, 7-H), and 7.30—7.45 (6 H, m, 1-H and CH_2Ph) (Found: M^+, 362.1126. $C_{22}H_{18}O_5$ requires *M*, 362.1155). Similar treatment of compound (**29**) afforded compound (**6**) in 52% yield.

3-*Benzyloxy*-6H-[1,3]*dioxolo*[5,6]*benzofuro*[3,2-c][1]*benzopyran* (**9**).—A mixture of compound (**6**) (50 mg), CsF (105 mg), and CH_2Br_2 (27 mg) in DMF (3 ml) was heated at 100 °C with stirring under an argon atmosphere for 1 h. Water was added to the reaction mixture and the product was extracted with Et_2O. The organic extract was washed with water and brine, dried, and evaporated under reduced pressure. The residue was subjected to preparative thin layer chromatography to afford the title compound as colourless crystals (32 mg, 63%), m.p. 164—165 °C (benzene) (lit.,[15] m.p. 167—168 °C) (Found: C, 74.3; H, 4.3. $C_{23}H_{16}O_5$ requires C, 74.18; H, 4.33%); $\nu_{max.}$(KBr) 1 624, 1 588, and 1 504 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 5.06 (2 H, s, CH_2Ph), 5.51 (2 H, s, 6-H_2), 5.98 (2 H, s, 9-H_2), 6.58 (1 H, d, *J* 2.5 Hz, 4-H), 6.60 (1 H, dd, *J* 2.5 and 8.5 Hz, 2-H), 6.73 (1 H, d, *J* 0.5 Hz, 11-H), 7.01 (1 H, d, *J* 0.5 Hz, 7-H), and 7.31—7.46 (6 H, m, CH_2Ph and 1-H) (Found: M^+, 372.0980. $C_{23}H_{16}O_5$ requires *M*, 372.0998).

cis-3a,9b-*Dihydro*-7-*methoxy*-3-*methylene*-4H-*furo*[3,2-c]-[1]*benzopyran*-2(3H)-*one* (**11**).—Compound (**11**) was obtained from *cis*-3a,9b-dihydro-7-methoxy-4*H*-furo[3,2-*c*][1]benzopyran-2(3*H*)-one (**13**) in the same manner as for compound (**10**) in 60% yield, m.p. 93—94 °C (Et_2O) (Found: C, 66.95; H, 5.3. $C_{13}H_{12}O_4$ requires C, 67.23; H, 5.21%); $\nu_{max.}$(KBr) 1 752, 1 626, and 1 590 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 3.4—4.5 (3 H, m, 3a-H and 4-H_2), 3.73 (3 H, s, OMe), 5.33 (1 H, d, *J* 6 Hz, 9b-H), 5.72, 6.33 (each 1 H, d, *J* 1 Hz, =CH_2), 6.39 (1 H, d, *J* 3 Hz, 6-H), 6.52 (1 H, dd, *J* 3 and 8 Hz, 8-H), and 7.25 (1 H, d, *J* 8 Hz, 9-H) (Found: M^+, 232.0740. $C_{13}H_{12}O_4$ requires *M*, 232.0736).

cis-4-*Hydroxy*-7-*methoxychroman*-3-*yl*-3,3-*bis*(*ethylthio*)-6-*hydroxycyclohex*-5-*en*-4-*one* (**28**) *and* cis-4-*Hydroxy*-7-*methoxychroman*-3-*yl*-3,3-*bis*(*ethylthio*)*cyclohexan*-4,6-*dione* (**30**).—A solution of ketone (**15**) (2.14 g) in DME (10 ml) was added to a suspension of NaH (0.22 g) in DME (10 ml) with stirring at 0 °C. The mixture was stirred for 15 min at room temperature and then a solution of compound (**11**) (2.32 g) in DME (20 ml) was added to it at 0 °C. Stirring was continued for 8 h at room temperature, and then NaH (0.22 g) was added to the solution at 0 °C and stirring was continued for a further 16 h at room temperature. Solvent was evaporated under reduced pressure then water was added to the residue and the solution was washed with ether. The water layer was acidified with 10% HCl and extracted with CH_2Cl_2. The organic extract was washed with water and brine, dried, and evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel with 1% (v/v) MeOH–CH_2Cl_2 to give compounds (**28**) and (**30**). *Compound* (**28**) (1.63 g, 40%), m.p. 132—135 °C, $\nu_{max.}$($CHCl_3$) 3 500, 1 625, and 1 580 cm^{-1}; δ_H(60 MHz; 5% CD_3OD–$CDCl_3$) 1.13 (3 H, t, *J* 7 Hz, CH_2CH_3), 1.26 (3 H, t, *J* 7 Hz, CH_2CH_3), 2.2—2.8 (5 H, m, 2 × SCH_2 and 2-H), 3.1—3.6 (1 H, m, 1-H), 3.73 (3 H, s, OMe), 4.20 (2 H, br s, 2′-H_2), 5.33 (1 H, d, *J* 1 Hz, 5-H), 5.70 (1 H, d, *J* 7 Hz, 4′-H), 6.33 (1 H, d, *J* 3 Hz, 8′-H), 6.54 (1 H, dd, *J* 3 and 8 Hz, 6′-H), and 7.25 (1 H, d, *J* 8 Hz, 5′-H) (Found: M^+, 410.1224. $C_{20}H_{26}O_5S_2$ requires *M*, 410.1222). *Compound* (**30**) (0.32 g, 8%), m.p. 162—164 °C, $\nu_{max.}$($CHCl_3$) 3 580, 3 400, 1 708, and 1 620 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.19 (3 H, t, *J* 7.5 Hz, CH_2CH_3), 1.27 (3 H, t, *J* 7.5 Hz, CH_2CH_3), 1.96 (1 H, dd, *J* 14 and 14.5 Hz, 2-H), 2.30 (1 H, dd, *J* 5 and 14.5 Hz, 2-H), 2.5—2.7 (4 H, m, 2 × SCH_2), 2.96 (1 H, d, *J* 14.5 Hz, 5-H), 3.06 (1 H, m, 1-H), 3.08 (1 H, d, *J* 14.5 Hz, 5-H), 3.77 (3 H, s, OMe), 3.93 (1 H, dd, *J* 10 and 11.3 Hz, 2′-$H_{ax.}$), 4.15 (1 H, dd, *J* 4.6 and 11.3 Hz, 2′-$H_{eq.}$), 4.80 (1 H, br s, OH), 5.13 (1 H, d, *J* 6 Hz, 4′-H), 6.42 (1 H, d, *J* 2.6 Hz, 8′-H), 6.56 (1 H, dd, *J* 2.6 and 8.5 Hz, 6′-H), and 7.24 (1 H, d, *J* 8.5 Hz, 5′-H) (Found: M^+, 410.1225. $C_{20}H_{26}O_5S_2$ requires *M*, 410.1222).

cis-6a,11a-*Dihydro*-3-*methoxy*-6H-*benzofuro*[3,2-c][1]*benzopyran*-8,9-*diol* (**7**).—Compound (**7**) was obtained from compounds (**28**) and (**30**) in the same manner as for compound (**6**) in 55% and 51% yield, respectively; m.p. 196—198 °C (benzene) (Found: C, 66.85; H, 4.65. $C_{16}H_{14}O_5$ requires C, 67.12; H, 4.93%); $\nu_{max.}$(KBr) 3 484, 3 372, 1 624, and 1 582 cm^{-1}; δ_H(270 MHz; 5% CD_3OD—$CDCl_3$) 3.46 (1 H, m, 6a-H), 3.61 (1 H, dd, *J* 10 and 10 Hz, 6-H_{ax}), 3.79 (3 H, s, OMe), 4.24 (1 H, dd, *J* 4.7 and 10 Hz, 6-$H_{eq.}$), 5.43 (1 H, d, *J* 6.7 Hz, 11a-H), 6.42 (1 H, s, 10-H), 6.47 (1 H, d, *J* 2.6 Hz, 4-H), 6.63 (1 H, dd, *J* 2.6 and 8.5 Hz, 2-H), 6.77 (1 H, s, 7-H), and 7.40 (1 H, d, *J* 8.5 Hz, 1-H) (Found: M^+, 286.0854. $C_{16}H_{14}O_5$ requires *M*, 286.0842).

3-*Methoxy*-6H-[1,3]*dioxolo*[5,6]*benzofuro*[3,2-c][1]*benzopyran* (*Anhydropisatin, Flemichapparin-B*) (**8**).—Compound (**8**) was obtained from compound (**7**) in the same manner as for compound (**9**) in 68% yield as colourless crystals, m.p. 183—185 °C (MeOH) (lit.,[16] m.p. 184—186 °C), $\nu_{max.}$(KBr) 1 654, 1 610, 1 572, and 1 512 cm^{-1}; $\lambda_{max.}$(EtOH) 324sh (log ε 4.06), 340 (4.28), and 358 (4.28); δ_H(270 MHz; $CDCl_3$) 3.80 (3 H, s, OMe), 5.51 (2 H, s, 6-H_2), 5.98 (2 H, s, 9-H_2), 6.49 (1 H, d, *J* 2.5 Hz, 4-H), 6.53 (1 H, dd, *J* 2.5 and 8.2 Hz, 2-H), 6.72 (1 H, d, *J* 0.5 Hz, 10-H), 7.01 (1 H, d, *J* 0.5 Hz, 7-H), and 7.36 (1 H, d, *J* 8.2 Hz, 1-H) (Found: M^+, 296.0671. $C_{17}H_{12}O_5$ requires *M*, 296.0685).

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