New Chromones from *Spathelia sorbifolia* L. (Rutaceae); Synthesis of the Benzo[1,2-*b*:3,4-*b'*]dipyranone Sorbifolin

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Ten more chromones containing both 2,2-dimethylchromen and 2-methylchromone entities, all derivatives of 5,7-dihydroxy-2-methylchromone, have been isolated from *Spathelia sorbifolia* L. and characterised. These are allopteroxylin (6), spatheliachromen (9), spatheliabischromen (4), methylallopteroxylin (8), methylsorbifolin (2), methylisospatheliachromen (19), anhydrosorbifolin (33), 6-(3-methylbut-2-enyl)allopteroxylin (28), 10-(3-methylbut-2-enyl)spatheliachromen (21), and 10-(3-methylbut-2-enoyl)spatheliachromen (23). Sorbifolin (1) has been synthesised *via* the reaction of singlet oxygen with the acetate of (28).

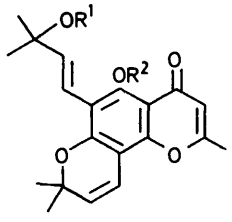
OUR initial investigation of *Spathelia sorbifolia* L. (Rutaceae) led to the isolation of the novel chromone sorbifolin (1).[1] Subsequent work on this species yielded a seco-ring A limonoid,[2] two 2-quinolones,[3] and several chromones. We now present a full account of our work on these last compounds,[4] and report the synthesis of sorbifolin (1).

The initial extraction [1] of the roots of *S. sorbifolia* gave a thick oil from which sorbifolin (1) could be easily crystallised. However, a similarly obtained extract from roots which had been kept for several weeks before extraction could not be crystallised, and t.l.c. showed the presence of many constituents. These were separated by preparative t.l.c. on silica gel.

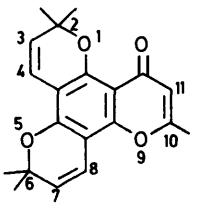
The major component (R_F *ca.* 0.25), $C_{20}H_{20}O_4$, had i.r. absorption appropriate for a chromone (1 660, 1 625, and 1 580 cm^{-1}), indicating a possible relationship with sorbifolin (1). The n.m.r. spectrum showed the chromone C-2 methyl signal as a broad singlet at δ 2.26, presumably coupled to a broad singlet for H-3 at 5.96, and revealed that the other protons were all accounted for by two 2,2-dimethylpyran systems. The two pyran 3-protons gave superimposed doublets at δ 5.60 (J 10 Hz) but the spectrum of a concentrated solution (*ca.* 20%) showed one of the 3-proton signals at 5.58. This bischromen was therefore assigned the structure (4) and called spatheliabischromen. This structure was confirmed by hydrogenation to the previously reported [1] anhydrotetrahydrosorbifolin (5). A compound of structure (4) had been

[1] W. R. Chan, D. R. Taylor, and C. R. Willis, *J. Chem. Soc.* (*C*), 1967, 2540.
[2] B. A. Burke, W. R. Chan, and D. R. Taylor, *Tetrahedron*, 1972, **28**, 425.
[3] C. D. Adams, D. R. Taylor, and J. M. Warner, *Phytochemistry*, 1973, **12**, 1359; R. Storer, D. W. Young, D. R. Taylor, and J. M. Warner, *Tetrahedron*, 1973, **29**, 1721.
[4] Preliminary publication, D. R. Taylor and J. A. Wright, *Rev. Latinoamer. Quim.*, 1971, **2**, 84.

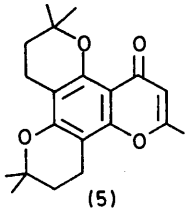
isolated previously [5] from an unnamed species of *Spathelia*; more recently, spatheliabischromen (4) has been isolated from *Cneorum tricoccum*.[6,7]



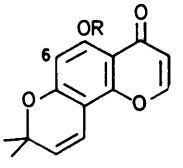
(1) $R^1 = R^2 = H$
(2) $R^1 = H$, $R^2 = Me$
(3) $R^1 = Me$, $R^2 = H$



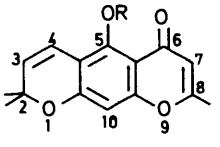
(4)



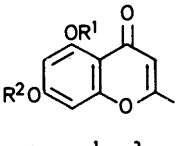
(5)



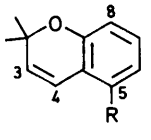
(6) R = H
(7) R = Ac
(8) R = Me



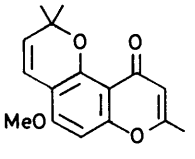
(9) R = H
(10) R = Ac
(11) R = Me
(12) R = $CH_2 \cdot CH : CMe_2$



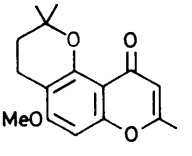
(13) $R^1 = R^2 = H$
(14) $R^1 = H$, $R^2 = CMe_2 \cdot C : CH$
(15) $R^1 = Ac$, $R^2 = CMe_2 \cdot C : CH$
(16) $R^1 = H$, $R^2 = Me$



(17) R = OH
(18) R = OAc



(19)



(20)

The second most abundant constituent was a yellow crystalline compound, $C_{15}H_{14}O_4$ (M^+ 258), m.p. 153—155°, whose i.r. spectrum shows hydroxylic absorption in addition to bands ascribable to a chromone. The presence of 2,2-dimethylchromen and 2-methylchromone systems could be deduced from the n.m.r. spectrum, which also revealed an aromatic proton singlet (δ 6.24) and a chelated phenolic proton (12.81). These data and the close correspondence of the u.v. spectra indicated that this compound was allopteroxylin (6), previously isolated from *Ptaeroxylon obliquum*.[8]

The preparative t.l.c. also provided an isomer of allopteroxylin (6), spatheliachromen, which was also yellow and whose spectral data revealed the same functional groups as in (6). On the assumption that it was also a derivative of 5,7-dihydroxy-2-methylchromone (13), spatheliachromen was assigned the structure (9), and this was confirmed by synthesis by the method of Hlubucek *et al.*[9] Thus, 5,7-dihydroxy-2-methylchromone (13) [10] was converted into the prop-2-ynyl ether (14) on treatment with 3-chloro-3-methylbut-1-yne [11] in the presence of potassium carbonate. Heating the ether (14) just above its m.p., in the absence of solvent, for 1 h gave a mixture (*ca.* 1 : 1) which was separated by preparative t.l.c. into spatheliachromen (9) and allopteroxylin (6), identical with the natural products. A similar, but independent, synthesis of (6) and (9) was simultaneously reported by Seshadri and his co-workers,[12] who, however, carried out the thermal rearrangement of (14) in *NN*-dimethylaniline.* Allopteroxylin (6) had been synthesised previously by another route.[14] We have found that protection of the phenol in (14) gives a greater proportion of (6) in the rearrangement product, presumably by removing chelation stabilisation and hence increasing the importance of 4-pyrone stabilisation of the transition state.[15] Thus, acetylation of (14), thermolysis of the non-crystalline acetate (15), and hydrolysis of the crude product gave a 2 : 1 mixture (n.m.r.) of allopteroxylin (6) and spatheliachromen (9).

The mass spectra of (6) and (9) show the fragmentation expected for the 2,2-dimethylchromen [16] and 2-methylchromone moieties.[17] In addition, they both show a significant doubly charged $M - CH_3$ ion at *m/e* 121.5 [18] which, in the case of (9), is the third most abundant ion (8%). Doubly charged ions in the mass spectra of (4) and (6) have been noted recently.[19]

It has been shown [20] that acetylation of a 5-hydroxy-2,2-dimethylchromen (17) [to give (18)] causes a marked

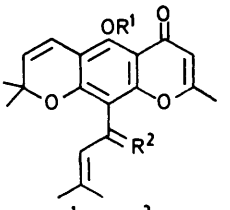
* Spatheliachromen (9) had also been prepared by another route and called ' dehydroisopeucenin,'[13] but had not been previously found in nature.

[5] Dr. N. Neuss, personal communication.
[6] A. G. Gonzalez, B. M. Fraga, and R. Torres, *Anal. Quim.*, 1974, **70**, 91.
[7] A. G. Gonzalez, B. M. Fraga, and O. Pino, *Phytochemistry*, 1974, **13**, 2305.
[8] F. M. Dean and D. A. H. Taylor, *J. Chem. Soc.* (*C*), 1966, 114.
[9] J. Hlubucek, E. Ritchie, and W. C. Taylor, *Austral. J. Chem.*, 1971, **24**, 2347.
[10] K. C. Gulati, S. R. Seth, and K. Venkataraman, *J. Chem. Soc.*, 1934, 1765.
[11] G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *J. Amer. Chem. Soc.*, 1950, **72**, 3542.
[12] B. S. Bajwa, P. Lal, and T. R. Seshadri, *Indian J. Chem.*, 1971, **9**, 17.
[13] A. C. Jain, V. K. Khanna, P. Lal, and T. R. Sheshadri, *Indian J. Chem.*, 1970, **8**, 480.
[14] W. M. Bandaranayake, L. Crombie, and D. A. Whiting, *J. Chem. Soc.* (*C*), 1971, 811.
[15] D. G. Clarke, L. Crombie, and D. A. Whiting, *J.C.S. Perkin I*, 1974, 1007.
[16] C. S. Barnes and J. L. Occolowitz, *Austral. J. Chem.*, 1964, **17**, 975.
[17] M. M. Badawi, M. B. E. Fayez, T. A. Bryce, and R. I. Reed, *Indian J. Chem.*, 1967, **5**, 591.
[18] F. W. McLafferty, ' Interpretation of Mass Spectra,' Benjamin, New York, 1967, p. 49.
[19] A. G. Gonzalez, B. M. Fraga, and O. Pino, *Rev. Real Acad. Ciencias*, 1975, **69**, 347.
[20] A. Arnone, G. Cardillo, L. Merlini, and R. Mondelli, *Tetrahedron Letters*, 1967, 4201.

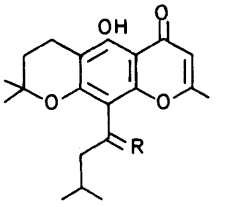
upfield shift of the chromen α-proton (H-4) signal and a smaller downfield shift of the β-proton (H-3) signal in the n.m.r. spectrum, whereas negligible shifts are shown on acetylation of 6-, 7-, and 8-hydroxy-2,2-dimethylchromens. In agreement, we have found that this technique can differentiate allopteroxylin (6) from spatheliachromen (9). Thus, conversion of (9) into the acetate (10) resulted in an upfield shift of the α-proton signal (0.20 p.p.m.) and a downfield shift of the β-proton signal (−0.14) ,whereas acetylation of (6) [to (7)] caused smaller downfield shifts of both α- (−0.08) and β- (−0.10) proton signals.

The band just below that containing spatheliabischromen (4) yielded, after further preparative t.l.c., sorbifolin (1) and a colourless crystalline compound, methylisospatheliachromen, $C_{16}H_{16}O_4$. The spectral properties of this compound showed it to be very similar to allopteroxylin (6) and spatheliachromen (9), except that a methyl group (δ 3.87) had replaced the phenolic proton. Again if we assume the presence of the 5,7-dihydroxy-2-methylchromone nucleus, three structures [(8), (11), and (19)] are possible for this methyl ether. Allopteroxylin (6), spatheliachromen (9), and their acetates (7) and (10) all show long-range coupling between the chromen α-proton and the aromatic proton. This coupling, manifested as only a broadening of the lower field doublet and the aromatic singlet in (6) and (7), occurs [20] only between H-4 and H-8 of the chromen system [chromen numbering; *cf.* (17)], and is absent in the n.m.r. spectrum of methylisospatheliachromen. Methylisospatheliachromen must therefore have structure (19); in agreement, it differs from the ethers (8) and (11), prepared from (6) and (9), respectively. A more detailed analysis of the n.m.r. spectrum further supports structure (19). The chemical shift of a chromen α-proton is dependent [21] on the substitution at C-5 [chromen numbering, *cf.* (17)]. In methylisospatheliachromen, this signal occurs at δ 6.60, indicating a phenolic or ether group at C-5. The shift of the aromatic proton signal (δ 6.31) shows that this proton cannot be placed *peri* to the carbonyl group and, taken with the above data, requires that methylisospatheliachromen be represented by (19). This was confirmed by hydrogenation to a dihydro-derivative (20), which was identical with methylallopeucenin [22] prepared by reaction of eugenin (16) [23] with 3-methylbut-2-enyl bromide and zinc chloride.

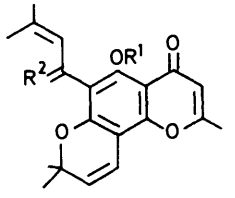
A similar extraction of *S. sorbifolia* stems yielded compounds (4), (6), (9), and (19) and two new compounds which, on the basis of the evidence outlined below, were identified as 10-(3-methylbut-2-enyl)spatheliachromen (21),* and 10-(3-methylbut-2-enoyl)spatheliachromen (23). Both give spectral data characteristic of 2,2-dimethylchromen and 2-methylchromone systems with a chelated phenol. In addition, the n.m.r. spectrum of the former (21) reveals a signal for two benzylic protons as a broadened doublet (*J* 6.5 Hz) at δ 3.38, an olefinic proton signal as a broad triplet at 5.20, and vinylic methyl signals as broadened singlets at 1.68 and 1.81. These data clearly indicate that a 3-methylbut-2-enyl group has replaced the aromatic proton of spatheliachromen (9) or allopteroxylin (6). Evidence in favour of the former possibility was provided by the upfield shift of the chromen α-proton signal (0.20 p.p.m.) and the downfield shift of the β-proton signal (−0.14) on



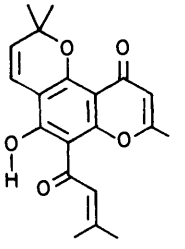
(21) R^1 = H R^2 = H_2
(22) R^1 = Ac, R^2 = H_2
(23) R^1 = H, R^2 = O
(24) R^1 = Ac, R^2 = O



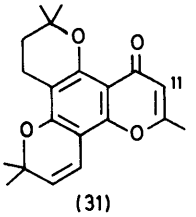
(25) R = O
(26) R = H_2



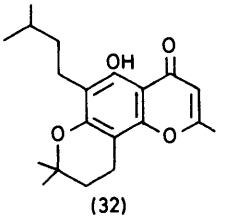
(27) R^1 = H, R^2 = O
(28) R^1 = H, R^2 = H_2
(29) R^1 = Ac, R^2 = H_2



(30)



(31)



(32)

acetylation [to (22)]. Structure (21) was confirmed by synthesis by Claisen rearrangement of spatheliachromen 3-methylbut-2-enyl ether (12) at 148 °C. The product (21) was accompanied by a smaller amount of spatheliachromen (9), formed by thermal cleavage. Compound (21) has also been subsequently found in *Neochamelae pulverulenta* [24] and *Cneorum tricoccum* [6,7] and has been synthesised recently by another route.[25]

The n.m.r. spectrum of 10-(3-methylbut-2-enoyl)-spatheliachromen (23) shows signals for vinylic methyl groups at δ 1.95 and 2.21 (doublets, *J* 1.1 and 1.3 Hz, respectively) and for an olefinic proton as a narrow multiplet at 6.33, indicating that the remaining five carbon atoms form a 3-methylbut-2-enoyl unit. Acetylation of

* Initially reported [4] as an oil but subsequently obtained crystalline.

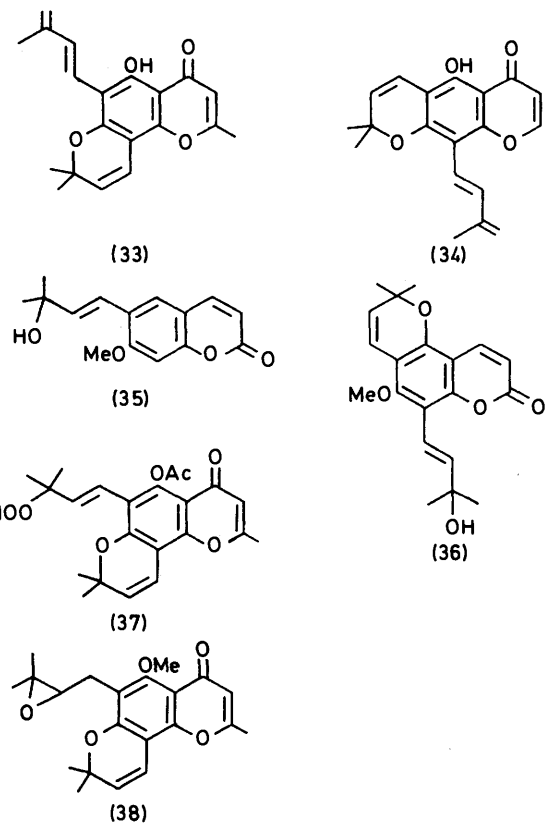
[21] T. Anthonsen, *Acta Chem. Scand.*, 1969, **23**, 3605.
[22] E. Spath and K. Eiter, *Ber.*, 1941, **74**, 1851.
[23] T. H. Meijer and H. Schmid, *Helv. Chim. Acta*, 1948, **31**, 1603.
[24] A. G. Gonzalez, J. P. Castaneda, and B. M. Fraga, *Anal. Quim.*, 1972, **68**, 447.
[25] A. Mondon and H. Callsen, *Chem. Ber.*, 1975, **108**, 2005.

(23) gave (24), the n.m.r. spectrum showing a concomitant upfield shift of the chromene α-proton signal (0.20 p.p.m.) and a downfield shift of the β-proton signal (−0.15). These data rule out the alternative structure (27) but not (30), which should also show a strongly chelated phenolic proton. However, the stability of the natural product to acid is not consistent with structure (27) or (30). both of which would readily cyclise under these conditions to a chroman-4-one.[26] Hydrogenation of (23) in glacial acetic acid over palladium–charcoal gave only the tetrahydro-derivative (25), but none of the hydrogenolysis product (26),* obtained by hydrogenation of (21). 10-(3-Methylbut-2-enoyl)spatheliachromen (23) appears to be only the second example [28] of a naturally occurring phenolic compound with a *C*-3-methylbut-2-enoyl unit.

In a later extraction of *S. sorbifolia*, the benzene extract was first subjected to column chromatography on alumina and the fractions were then further purified by preparative t.l.c. This improved procedure led to the isolation and characterisation of six more compounds. Two of these, the 2-quinolones *N*-methylflindersine and 4,7,8-trimethoxy-*N*-methyl-2-quinolone, have already been discussed.[3] The spectral data of the other four showed that they all contained 2,2-dimethylchromen and 2-methylchromone units. The simplest was identical with the methylallopteroxylin (8) prepared above, and has been found elsewhere in nature.[7,29] Another, $C_{21}H_{24}O_5$, had n.m.r. data very similar to those of sorbifolin (1) except that a methyl signal (δ 3.81) had replaced that due to the chelated phenolic proton. This compound, which could not be crystallised, must therefore be methylsorbifolin (2), and this was confirmed by comparison with the product of methylation of sorbifolin (1). The isomeric ether (3) [1] had also been isolated [30] but was shown to be an artefact.

The third chromone, $C_{20}H_{22}O_4$, is isomeric with 10-(3-methylbut-2-enyl)spatheliachromen (21) and its spectral data show it to have the same functionality. It was therefore identified as 6-(3-methylbut-2-enyl)allopteroxylin (28), and this was proven by the following evidence. Acetylation of (28) [to (29)] resulted in downfield shifts of both the chromen α- (−0.11) and β- (−0.14) proton signals as expected (see above) for a derivative of allopteroxylin (6). Furthermore, treatment of (28) with acid yielded the chroman (31), whereas the isomer (21) was unaffected by the same conditions. Hydrogenation of 6-(3-methylbut-2-enyl)allopteroxylin (28) afforded a tetrahydro-derivative (32), identical with hexahydrodeoxysorbifolin.[1]† The isomers (32) and (26) show slight differences in their spectra and can also be separated by t.l.c. on silica gel. Finally, reaction of allopteroxylin (6) with sodium hydride and 3-methylbut-2-enyl bromide in dry toluene under reflux [31] gave 6-(3-methylbut-2-enyl)-allopteroxylin (28) identical with the natural product. We have also isolated (28) from *S. glabrescens*,[32] and its synthesis by another route has recently appeared.[25]

The final chromone isolated from *S. sorbifolia*, $C_{20}H_{20}O_4$, showed n.m.r. signals for the 2,2-dimethylchromen



and 2-methylchromone systems, a chelated phenolic proton (δ 13.75), and the extra isoprenoid moiety at 2.01 (vinylic Me), 5.12 (C=CH_2), and 6.84 and 7.51 (1 H each, d, *J* 17 Hz). This C_5 unit is therefore a *trans*-3-methylbuta-1,3-dienyl group, and the compound was assigned the structure (33) since its m.p. and n.m.r. and u.v. data differed from those reported by Gonzalez *et al.*[24] for neochamelina, isolated from *Neochamelae pulverulenta* (*Cneorum pulverulentum*) and assigned structure (34) [24] and this was confirmed by hydrogenation of anhydrosorbifolin (33) to hexahydrodeoxysorbifolin (32). Anhydrosorbifolin (33) was obtained in good yield by dehydration of sorbifolin (1) with thionyl chloride. More recently, Mondon *et al.*[25] showed that cneorum-chromone G, isolated from *Cneorum pulverulentum*, had structure (33) and was probably identical with neochamelina. Gon-

* Not obtained crystalline by us, but recently reported [27] as having m.p. 80—81°.

† The material described previously [1] was found to be impure.

[26] *Cf.* M. Miyano and M. Matsui, *Bull. Chem. Soc. Japan*, 1958, **31**, 397; O. Dann, G. Volz, and O. Huber, *Annalen*, 1954, **587**, 16.

[27] A. Mondon, H. Callsen, P. Hartmann, G. Cuno, and C. H. Andersen, *Chem. Ber.*, 1975, **108**, 934.

[28] K. Hatta and A. Nitta, *J. Pharm. Soc. Japan*, 1957, **77**, 941.

[29] F. M. Dean and M. L. Robinson, *Phytochemistry*, 1971, **10**, 3221.

[30] W. R. Chan, D. R. Taylor, and C. R. Willis, unpublished results.

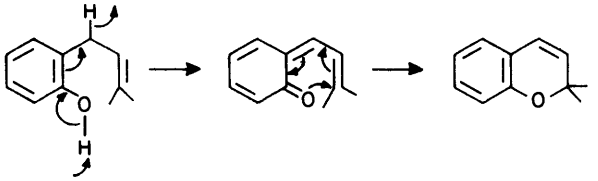
[31] J. Hlubucek, E. Ritchie, and W. C. Taylor, *Austral. J. Chem.*, 1971, **24**, 2355.

[32] V. G. Box and D. R. Taylor, *Phytochemistry*, 1973, **12**, 956.

zalez, Fraga, *et al.*[33a] have revised the structure of neochamelina to (33) without comment on its spectral data, and Mondon *et al.*[33b] have shown that authentic (34) has a much lower m.p. The spectral data for cneorumchromone G and anhydrosorbifolin are virtually identical, and the difference in m.p. may be due to crystallisation from different solvents.

In sorbifolin (1),[1] one of the isoprenoid units is a *trans*-3-hydroxy-3-methylbut-1-enyl group. This modification is rare in nature; the only other examples of which we are aware are in the coumarins suberenol (35) [34] and avicennol (36).[35] We have synthesised sorbifolin (1) *via* the hydroperoxide (37) formed by the reaction of photochemically generated singlet oxygen with 6-(3-methylbut-2-enyl)allopteroxylin acetate (29). An attempt to generate the *trans*-3-hydroxy-3-methylbut-1-enyl system by the reaction of the epoxymethyl ether (38) with base [36] failed.

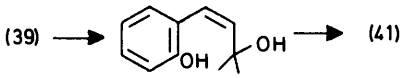
We have also achieved a synthesis of spatheliabischromen (4) by cyclodehydration of sorbifolin (1). This was accomplished in fair yield by treatment of (1) with sulphuric acid in acetic acid. The use of hydrochloric acid



SCHEME 1

in methanol gave [1] the solvolysis product (3), and treatment with thionyl chloride–pyridine in acetone (see above) yielded anhydrosorbifolin (33). Other syntheses of spatheliabischromen (4) have been reported recently,[25,37] and in view of these, the photolysis with sunlight through Pyrex of spatheliabischromen (4) in tetrahydrofuran–water to yield,[38] quantitatively, sorbifolin (1) constitutes an alternative route to sorbifolin.

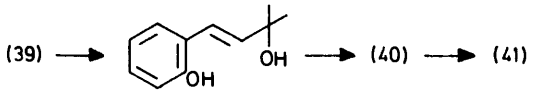
Two routes have been suggested for the *in vivo* conversion of *o*-3-methylbut-2-enylphenols [*e.g.* (39)] into 2,2-dimethylchromens. In the first, suggested by Ollis and Sutherland [39] and modified by Turner,[40] abstraction of benzylic hydride leads, after proton loss, to the *o*-quinone allylide (40) which cyclises to the chromen (41) (Scheme 1). Analogous *in vitro* conversions have been achieved with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.[41] The other route, due to Polonsky and her coworkers,[42] postulates the oxidation of the methylbutenyl unit to a *cis*-allylic alcohol [*e.g.* (42)], which can yield the 2,2-dimethylchromen by cyclodehydration (Scheme 2).



(42)

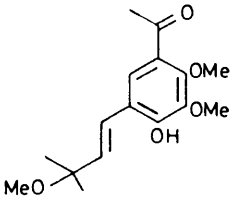
SCHEME 2

An *in vitro* conversion, ostensibly *via* this route, was reported.[42] However, the allylic alcohol formed from the hydroperoxide obtained by oxidation with singlet oxygen was probably *trans* and not *cis* as assumed.[42] The coincidence of the n.m.r. signals for the two olefinic protons [42] does not allow the geometry to be assigned, but

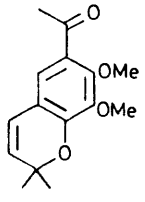


SCHEME 3

it has been shown in similar cases [43,44] that the *trans*-isomer is produced (see also above). A third possibility, Scheme 3, can be envisaged. In this connection, we have found,[38] that the allylic ether (43) slowly cyclises to the chromen (44) at room temperature in the dark. The observation that whereas freshly collected *S. sorbifolia* [1] and *S. glabrescens* [32] yielded mainly sorbifolin (1), samples of both plants which had been kept for several weeks gave mainly spatheliabischromen (4),[45] may be due to an *in vivo* conversion of (1) into (4) or may simply reflect the acid-catalysed reaction described above. In the former circumstance, the relative amounts of (1) and (4) in fresh plant material may be due to the photolysis of (4) to (1)



(43)



(44)

in vivo.[38,46] The rarity of *o*-*trans*-3-hydroxy-3-methylbut-1-enylphenols in nature, sorbifolin (1) being the only known example, may be due to their ready conversion into 2,2-dimethylchromens as suggested by Scheme 3.

[33] Personal communications from (*a*) B. M. Fraga; (*b*) A. Mondon.

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[46] *Cf.* J. Kolc and R. S. Becker, *Photochem. Photobiol.*, 1970, **12**, 383.

The relative stability of sorbifolin (1) is presumably due to chelation.

EXPERIMENTAL

U.v. spectra were obtained from ethanolic solutions and i.r. spectra for solutions in chloroform; n.m.r. spectra were recorded with a Varian A-60 spectrometer for solutions in deuteriochloroform (tetramethylsilane as internal standard) unless stated otherwise. Preparative t.l.c. was carried out on 1 mm thick plates of Merck $PF_{254+366}$ silica gel and column chromatography on Merck grade II–III alumina. Light petroleum was that of b.p. 60—80 °C.

Extraction.—(*a*) The finely ground roots of *Spathelia sorbifolia* (230 g) were extracted by percolation with benzene to give, after evaporation, a gum (5.9 g). Preparative t.l.c. of the crude extract (100 mg per 20 × 40 cm plate) in chloroform gave four bands. Band A (highest R_F) (380 mg) afforded, after further preparative t.l.c. in light petroleum–acetone (3 : 1), spatheliachromen (9) (70 mg) as yellow crystals from methanol, m.p. 139—141° (lit.,[13] 140—141°), $\nu_{max.}$ 3 350, 1 660, 1 615, and 1 585 cm^{-1}; $\lambda_{max.}$ 230, 249, 277, 303sh, and 322sh nm (ε 25 100, 22 350, 43 700, 13 050, and 7 000); δ 1.45 (6 H, s), 2.32br (3 H, s), 5.60 and 6.71 (1 H each, d, *J* 10 Hz, chromen β- and α-protons), 6.01br (1 H, s, H-7), 6.28 (1 H, s, H-10), and 13.06 (1 H, s, ArOH); *m/e* 258 (M^+, 17%), 257 (4), 243 (100), 217 (2), 203 (5), and 121.5 (8) (Found: C, 70.0; H, 5.6; O, 24.85. Calc. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.5; O, 24.8%). Band B (400 mg) gave, from methanol, yellow crystals (90 mg) of allopteroxylin (6), m.p. 153—155° (lit.,[8] 150—152°), $\nu_{max.}$ 3 270, 1 660, 1 608, and 1 585 cm^{-1}; $\lambda_{max.}$ 233, 239sh, 267, 301sh, and 349 (ε 18 150, 18 800, 32 700, 3 450, and 2 500); δ 1.46 (6 H, s), 2.36br (3 H, s), 5.57, and 6.67 (1 H each, d, *J* 10 Hz), 6.01br (1 H, s, H-3), 6.24 (1 H, s, H-6), and 12.81 (1 H, s, ArOH); *m/e* 258 (M^+, 15%), 243 (100), 203 (14), and 121.5 (5) (Found: C, 69.65; H, 5.4; O, 24.6. Calc. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.5; O, 24.8%). Band C (1.18 g) crystallised from ethyl acetate–light petroleum to give, as needles, *spatheliabischromen* (2,2,6,6,10-*pentamethyl*-2H,6H-*benzo*-[1,2-b : 3,4-b′ : 5,6-b″]*tripyran*-12-*one*) (4), m.p. 146—148.5°, $\nu_{max.}$ 1 660, 1 625, and 1 580 cm^{-1}; $\lambda_{max.}$ 224, 245, 273, 286, and 296 nm (ε 18 750, 22 200, 23 200, 22 850, and 19 400); δ 1.48 and 1.53 (6 H each, s), 2.26br (3 H, s), 5.60 (2 H, d, *J* 10 Hz), 5.96br (1 H, s, H-11), and 6.65 and 6.73 (1 H each, d, *J* 10 Hz) (Found: C, 74.4; H, 6.2; O, 19.65. $C_{20}H_{20}O_4$ requires C, 74.1; H, 6.2; O, 19.7%). Band D (1.35 g) was rechromatographed in benzene–ethyl acetate (2 : 1) to give sorbifolin (1) (100 mg) and O-*methylisospatheliachromen* (5-*methoxy*-2,2,8-*trimethyl*-2H-*benzo*[1,2-b : 3,4-b′]*dipyran*-10-*one*) (19) (50 mg), m.p. 143—145° (from ethyl acetate–light petroleum), $\nu_{max.}$ 1 660, 1 640, and 1 595 cm^{-1}; $\lambda_{max.}$ 224, 248sh, 254sh, 260sh, and 270 nm (ε 12 400, 9 700, 12 150, 14 850, and 18 000); δ 1.51 (6 H, s), 2.23br (3 H, s), 3.87 (3 H, s), 5.56 and 6.60 (1 H each, d, *J* 10 Hz), 5.92br (1 H, s, H-9), and 6.31 (1 H, s, H-6) (Found: C, 70.6; H, 5.9%; M^+ 272. $C_{16}H_{16}O_4$ requires C, 70.6; H, 5.9%; *M*, 272).

(*b*) A similar extraction of *S. sorbifolia* stems (290 g) gave a gum (7 g) which was separated by preparative t.l.c. into five bands. Band A (highest R_F) (590 mg) was rechromatographed in light petroleum–acetone (3 : 1) to yield spatheliachromen and 10-(3-*methylbut*-2-*enyl*)*spatheliachromen* (21) (80 mg), m.p. 94—96° (from methanol–water), $\nu_{max.}$ 3 250, 1 660, 1 625, and 1 585 cm^{-1}; $\lambda_{max.}$ 229, 260 sh, and 279 nm (ε 17 700, 16 250, and 26 400); δ 1.45 (6 H, s), 1.68br (3 H, s, $W_{\frac{1}{2}}$ 4 Hz), 1.81br (3 H, s. $W_{\frac{1}{2}}$ 3 Hz). 2.35br (3 H. s), 3.38br (2 H, d, *J* 6.5 Hz), 5.20br (1 H, t, *J* 6.5 Hz), 5.60 and 6.71 (1 H each, d, *J* 10 Hz), 6.00br (1 H, s, H-7) and 13.00 (1 H, s, ArOH) (Found: C, 73.8; H, 6.7. $C_{20}H_{22}O_4$ requires C, 73.6; H, 6.8%). The *acetate* (22) has $\nu_{max.}$ 1 760, 1 650, and 1 595 cm^{-1}; δ 1.47 (6 H, s), 1.69br and 1.81br (3 H each, s), 2.31br (3 H, s), 2.43 (3 H, s, OAc), 3.46br (2 H, d, *J* 7 Hz), 5.21br (1 H, t, *J* 7 Hz), 5.74 and 6.51 (1 H each, d, *J* 10 Hz), and 5.96br (1 H, s, H-7). Band B afforded mainly allopteroxylin (6). Band C (500 mg) yielded, after further preparative t.l.c. in benzene, 10-(3-*methylbut*-2-*enoyl*)*spatheliachromen* (23) (320 mg), m.p. 135—136.5° (from light petroleum), $\nu_{max.}$ 3 300, 1 660, 1 620, and 1 585 cm^{-1}; $\lambda_{max.}$ 220sh, 243sh, 248, 254, 260, 276, and 350sh nm (ε 19 400, 24 600, 27 000, 28 800, 29 800, 39 500, and 3 400); δ 1.46 (6 H, s), 1.95 (3 H, d, *J* 1.1 Hz), 2.21 (3 H, d, *J* 1.3 Hz), 2.31br (3 H, s), 5.62 and 6.71 (1 H each, d. *J* 10 Hz), 6.03br (1 H, s, H-7), 6.33 (1 H, m, $W_{\frac{1}{2}}$ 4 Hz), and 13.36 (1 H, s, ArOH) (Found: C, 70.3; H, 5.8%; M^+, 340. $C_{20}H_{20}O_5$ requires C, 70.6; H, 5.9%; *M*, 340). The *acetate* (24) has $\nu_{max.}$ 1 765, 1 655, 1 605, and 1 580 cm^{-1}; δ 1.47 (6 H, s), 1.97 (3 H, d, *J* 1.1 Hz), 2.26 (6 H, C-8 CH_3 and vinylic CH_3), 2.46 (3 H, s, OAc), 5.77 and 6.51 (1 H each, d, *J* 10 Hz), 5.97br (1 H, s, H-7), and 6.33 (1 H, m) (Found: C, 69.4; H, 6.0. $C_{22}H_{22}O_6$ requires C, 69.1; H, 5.8%). Bands D and E gave mainly spatheliabischromen and methylisospatheliachromen.

(*c*) The residue (5.8 g) from a later benzene extraction of old roots (200 g) was chromatographed on an alumina (400 g) column and eluted with benzene (300 ml), benzene–ethyl acetate (9 : 1, 250 ml; 1 : 1, 250 ml). and ethyl acetate–methanol (4 : 1, 450 ml). Fractions (50 ml) were collected and subjected to preparative t.l.c. in benzene–acetone (10 : 1) as necessary to yield, in addition to the compounds described above, the following. Fraction 3 gave *N*-methylflindersine [3] (32 mg). Fractions 13—16 afforded *N*-methyl-4,7,8-trimethoxy-2-quinolone [3] (30 mg). Fractions 17—23 yielded methylallopteroxylin (8) (97 mg), identical with the material described below, and 5-O-*methylsorbifolin* (2) (175 mg), $\nu_{max.}$ 3 330, 1 647, 1 616, and 1 572 cm^{-1}; $\lambda_{max.}$ 245, 252, 268, and 325 nm (ε 24 700, 27 200, 42 000, and 5 400); δ 1.47 and 1.53 (6 H each, s), 2.20 (1 H, s, OH), 2.33br (3 H, s), 3.81 (3 H, s, OCH_3), 5.73 and 6.83 (1 H each, d, *J* 10 Hz), 6.08br (1 H, s, H-3) and 6.74 and 6.88 (1 H each, d, *J* 17 Hz) (Found: M^+ 356.1622. $C_{21}H_{24}O_5$ requires *M*, 356.1662).

(*d*) The residue (4.2 g) from a similar extraction of old stems (200 g) was chromatographed on alumina (350 g) and eluted with light petroleum–ethyl acetate (3 : 2, 700 ml; 1 : 1, 400 ml; 3 : 7, 300 ml), ethyl acetate (250 ml), and ethyl acetate–methanol (1 : 1, 250 ml). Fractions (50 ml) were collected and two new compounds were isolated. Preparative t.l.c. of fractions 3—9 in benzene–acetone (10 : 1) yielded 6-(3-*methylbut*-2-*enyl*)*allopteroxylin* (28) (44 mg), m.p. 99—101.5° (from methanol– water), $\nu_{max.}$ 1 645, 1 594, and 1 575 cm^{-1}; $\lambda_{max.}$ 227, 241, 268, 301, 319, and 352 nm (ε 24 300, 19 650, 32 850, 2 650, 2 600, and 3 100); δ 1.45 (6 H, s), 1.67br and 1.79br (3 H each, s), 2.33br (3 H, s), 3.30br (2 H, d, *J* 7 Hz), 5.21br (1 H, t, *J* 7 Hz), 5.53 and 6.64 (1 H each, d, *J* 10 Hz), 5.97br (1 H, H-3), and 13.03 (1 H, s, ArOH) (Found: C, 72.9; H, 7.0. $C_{20}H_{22}O_4$, $0.25H_2O$ requires C, 72.6; H, 6.85%), and *anhydrosorbifolin* (33) (40 mg), m.p. 150—152.5° (from ethyl acetate–light petroleum), $\nu_{max.}$ 1 645 and 1 580 cm^{-1}; $\lambda_{max.}$ 222, 226, 251, 284, 290, 304, and 347 nm (ε 18 800, 19 700, 26 500, 36 200, 36 500, 26 500, and 3 500); δ 1.51 (6 H, s), 2.01br (3 H, s, $W_{\frac{1}{2}}$ 3 Hz), 2.37br (3 H, s), 5.12br (2 H, s, $W_{\frac{1}{2}}$ 4 Hz), 5.61 and 6.70 (1 H each, d. *J* 10 Hz). 6.05br (1 H. s. H-3), 6.84 and 7.51

(1 H each, d, J 17 Hz) and 13.75 (1 H, s, ArOH) (Found: C, 74.0; H, 6.3. $C_{20}H_{20}O_4$ requires C, 74.05; H, 6.2%).

Hydrogenation of Spatheliabischromen (4).—A mixture of pre-reduced 10% palladium–charcoal (63 mg) and spatheliabischromen (4) (59 mg) in ethanol (15 ml) was shaken in hydrogen. The reaction was complete after 30 min. The product, which crystallised from methanol–water (m.p. 154—155°), was identical with authentic anhydrotetrahydrosorbifolin (5) [1] (m.p., mixed m.p., and spectra).

Synthesis of Spatheliachromen (9) *and Allopteroxylin* (6).—A mixture of 5,7-dihydroxy-2-methylchromone (13) [10] (474 mg), 3-chloro-3-methylbut-1-yne [11] (2.26 g), and an excess of potassium iodide and anhydrous potassium carbonate in dry acetone (120 ml) was heated under reflux. After 100 h (t.l.c. control), the solids were filtered off and the solution was concentrated *in vacuo*. Dilution with water and extraction into chloroform gave the crude product (967 mg), which was purified by chromatography on alumina to yield the *prop-2-ynyl ether* (14) (396 mg), m.p. 149—151.5° (from methanol), $\nu_{max.}$ 3 205, 1 660, 1 625, and 1 585 cm^{-1}; $\lambda_{max.}$ 217sh, 230, 251, 257, 290, and 314sh nm (ε 13 650, 15 650, 17 550, 17 550, 6 700, and 4 450); δ 1.71 (6 H, s), 2.34br (3 H, s), 2.69 (1 H, s), 6.01br (1 H, s, H-3), 6.63 and 6.75 (1 H, each, d, J 2 Hz), and 12.63 (1 H, s, ArOH) (Found: C, 69.7; H, 5.4; O, 24.8. $C_{15}H_{14}O_4$ requires C, 69.75; H, 5.5; O, 24.8%). The ether (14) was heated at 153—157 °C for 1 h to give a mixture of spatheliachromen (9) and allopteroxylin (6) (1 : 1 by n.m.r.), which were separated by preparative t.l.c. and compared with the natural products.

The ether (14) was converted into the *acetate* (15), $\nu_{max.}$ 1 760, 1 655, and 1 610 cm^{-1}; δ 1.73 (6 H, s), 2.30br (3 H, s), 2.40 (3 H, s, OAc), 2.78 (1 H, s), 5.98br (1 H, s, H-3), and 6.78 and 7.23 (1 H each, J 2.5 Hz). Thermal rearrangement of (15) for 1 h at 155 °C was followed by hydrolysis of the acetate with dilute hydrochloric acid in methanol to give a mixture of (6) and (9) (2 : 1 by n.m.r.), from which the pure compounds were isolated by preparative t.l.c.

Spatheliachromen Acetate (10).—The *acetate* (10), prepared from spatheliachromen (9) with acetic anhydride and pyridine at room temperature for 2 days, has m.p. 143—144° (from methanol), $\nu_{max.}$ 1 765, 1 655, 1 610, and 1 565 cm^{-1}; $\lambda_{max.}$ 233, 260. 323, and 333 nm (ε 18 800, 40 100, 8 200. and 8 500); δ 1.47 (6 H, s), 2.28br (3 H, s), 2.44 (3 H, s, OAc), 5.74 and 6.51 (1 H each, d, J 10 Hz), 5.95br (1 H, s, H-7), and 6.68 (1 H, s, H-10) (Found: C, 68.1; H, 5.5. $C_{17}H_{16}O_5$ requires C, 68.0; H, 5.4%).

Allopteroxylin Acetate (7).—The *acetate* (7), prepared from (6) as above, has m.p. 145—146° (from ethyl acetate–light petroleum), $\nu_{max.}$ 1 760, 1 655, 1 600, and 1 570 cm^{-1}; $\lambda_{max.}$ 236, 257sh, 264, and 311 nm (ε 29 450, 36 450, 38 700, and 6 000); δ 1.48 (6 H, s), 2.32br (3 H, s), 2.40 (3 H, s, OAc), 5.67 and 6.75 (1 H each, d, J 10 Hz), 5.98br (1 H, s, H-3), and 6.47 (1 H, s, H-6) (Found: C, 67.95; H, 5.4. $C_{17}H_{16}O_5$ requires C, 68.0; H, 5.4%).

O-*Methylallopteroxylin* (8).—The *methyl ether* (8) was prepared by the reaction of allopteroxylin (6) with an excess of methyl iodide and potassium carbonate in dry acetone under reflux for 2.5 h and has m.p. 152.5—154° (from ethyl acetate–light petroleum), $\nu_{max.}$ 1 660, 1 615, and 1 575 cm^{-1}; $\lambda_{max.}$ 223, 241sh, 253sh, 263, 298sh, and 334 nm (ε 14 500, 19 400, 30 000, 34 900, 4 500, and 4 100); δ 1.48 (6 H, s), 2.29br (3 H, s), 3.93 (3 H, s, OCH_3), 5.56 and 6.71 (1 H each, d, J 10 Hz), 6.01br (1 H, s, H-3), and 6.31 (1 H, s, H-6) (Found: C, 70.7: H. 6.0. $C_{16}H_{16}O_4$ requires C, 70.6; H, 5.9%).

O-*Methylspatheliachromen* (11).—Prepared from (9) as above, the *ether* (11) has m.p. 120—122° (from ethyl acetate–light petroleum), $\nu_{max.}$ 1 655, 1 605, and 1 560 cm^{-1}; $\lambda_{max.}$ 227sh, 234, 253sh, 264, and 328 nm (ε 13 300, 13 750, 25 500, 29 900, and 4 950); δ 1.47 (6 H, s), 2.28br (3 H, s), 3.90 (3 H, s, OCH_3), 5.71 and 6.75 (1 H each, d, J 10 Hz), 6.00br (1 H, s, H-7), and 6.58 (1 H, s, H-10) (Found: C, 70.35; H, 6.0. $C_{16}H_{16}O_4$ requires C, 70.6; H, 5.9%).

O-*Methylallopeucenin* (*Dihydro-O-methylisospatheliachromen*) (20).—(*a*) 5,7-Dihydroxy-2-methylchromone (13) (213 mg) was methylated in methanol with dimethyl sulphate (2 ml) and 2N-sodium hydroxide (18 ml). The crude product was separated by preparative t.l.c. into eugenin (16) (62 mg), m.p. 105—108° (from methanol) (lit.,[23] 115—117°), $\nu_{max.}$ 3 200, 1 660, 1 620, and 1 585 cm^{-1}; δ 2.33br (3 H, s), 3.85 (3 H, s), 6.03br (1 H, s, H-3), 6.33 (2 H, s), and 12.76 (1 H, s, ArOH), and *O*-methyleugenin (84 mg), m.p. 124—125° (from ethyl acetate–light petroleum), $\nu_{max.}$ 1 658, 1 610, and 1 575 cm^{-1}; δ 2.26br (3 H, s), 3.88 (3 H, s), 3.95 (3 H, s), 6.02br (1 H, s, H-3), and 6.36 and 6.45 (1 H each, d, J 2 Hz), M^+ 220. A mixture of 3-methylbut-2-enyl bromide (120 mg), eugenin (16) (59 mg), and an excess of freshly fused zinc chloride in dry benzene (30 ml) was heated under reflux for 30 h. The cooled solution was decanted, washed with water, aqueous 5% sodium hydrogen carbonate, and water, and evaporated. Preparative t.l.c. of the residue yielded unchanged eugenin (12 mg) and *O*-methylallopeucenin (20) (23 mg), m.p. 168—170° (from ethyl acetate–light petroleum) (lit.,[22] 170—171°), $\nu_{max.}$ 1 658 and 1 597 cm^{-1}; $\lambda_{max.}$ 216, 238, 252infl, 288 and 312sh nm (ε 20 900, 20 350, 19 900, 9 750, and 5 950); δ 1.41 (6 H, s), 1.80 (2 H, t, J 7 Hz), 2.26br (3 H, s), 2.65 (2 H, t, J 7 Hz), 3.90 (3 H, s), 5.98br (1 H, s, H-9), and 6.38 (1 H, s) (Found: C, 70.1; H, 6.6. Calc. for $C_{16}H_{18}O_4$: C, 70.1; 6.6%).

(*b*) Hydrogenation of *O*-methylisospatheliachromen (19) (44 mg) in ethanol (20 ml) over 10% palladium–charcoal (35 mg) gave, after 2 h, dihydro-*O*-methylisospatheliachromen (*O*-methylallopeucenin) (20) identical with the synthetic product described above.

Synthesis of 10-(3-*Methylbut-2-enyl*)*spatheliachromen* (21).—3-Methylbut-2-enyl bromide (66 mg) was added to spatheliachromen (9) (75 mg) and sodium hydride (36 mg) in dry benzene (25 ml) and the mixture was heated under reflux for 3.5 h. The excess of sodium hydride was destroyed by adding glacial acetic acid to the cooled mixture, which was then diluted with chloroform and washed with water. The crude product (101 mg) was separated by preparative t.l.c. in chloroform into unchanged (9) and the *ether* (12) (36 mg), m.p. 119—122° (from light petroleum), $\nu_{max.}$ 1 655 and 1 603 cm^{-1}; δ 1.46 (6 H, s), 1.71br and 1.78br (3 H each, s), 2.28br (3 H, s), 4.59br (2 H, d, J 7.5 Hz), 5.66br (1 H, t, J 7.5 Hz), 5.71 and 6.80 (1 H each, d, J 10 Hz), 6.03br (1 H, s, H-7), and 6.61 (1 H, s) (Found: C, 72.9; H, 6.8. $C_{20}H_{22}O_4$ requires C, 73.6; H, 6.8%). The ether (12) was rearranged by heating at 148 °C for 2 h, and the crude product, a mixture of (9) and (21) (1 : 1 by n.m.r.), was separated by preparative t.l.c. in light petroleum–acetone (3 : 1). The product (21) was shown to be identical with the natural product by the usual criteria.

Hydrogenation of 10-(3-*Methylbut-2-enyl*)*spatheliachromen* (21).—Hydrogenation of (21) (42 mg) in ethanol (25 ml) over 10% palladium–charcoal (70 mg) for 1 h gave the *tetrahydroderivative* (26), $\nu_{max.}$ 1 656, 1 618, and 1 585 cm^{-1}, δ 0.96 (6 H, d, J 5.5 Hz), 1.36 (6 H, s), *ca.* 1.21—1.59 (3 H, m), 1.81 (2 H, t, J 6.5 Hz), 2.36br (3 H, s), 2.55—2.80 (2 H, m), 2.72 (2 H,

t, *J* 6.5 Hz), 6.03br (1 H, s, H-7), and 13.03 (1 H, s, ArOH) (Found: C, 72.9; H, 8.1. $C_{20}H_{26}O_4$ requires C, 72.7; H, 7.9%).

Hydrogenation of 10-(3-*Methylbut*-2-*enoyl*)*spatheliachromen* (23).—Hydrogenation of (23) (46 mg) in glacial acetic acid (50 ml) over 10% palladium–charcoal (47 mg) for 8 h yielded the *tetrahydro-derivative* (25), m.p. 117—119° (from light petroleum), $\nu_{max.}$ 1 685sh, 1 647, 1 610, and 1 582 cm^{-1}; δ 0.98 (6 H, d, *J* 6.5 Hz), 1.40 (6 H, s), 1.85 (2 H, t, *J* 6.5 Hz), *ca.* 2.3br (1 H, m), 2.33br (3 H, s), 2.71 (2 H, d, *J* 6 Hz), 2.74 (2 H, t, *J* 6.5 Hz), 6.08br (1 H, s, H-7), and 13.41 (1 H, s, ArOH) (Found: C, 69.9; H, 6.9. $C_{20}H_{24}O_5$ requires C, 69.75; H, 7.0%).

6-(3-*Methylbut*-2-*enyl*)*allopteroxylin Acetate* (29).—A solution of (28) (36 mg) in pyridine (1 ml) and acetic anhydride (1.5 ml) was set aside at room temperature for 5 weeks (t.l.c. control). The *acetate* (29) crystallised from light petroleum; m.p. 103—104°, $\nu_{max.}$ 1 750, 1 645, 1 618, and 1 585 cm^{-1}; $\lambda_{max.}$ 230, 236, 257, 264, and 320 nm (ε 27 100, 29 700, 30 300, 33 600, and 7 100); δ 1.48 (6 H, s), 1.68 and 1.78br (3 H each, s), 2.32br (3 H, s), 2.42 (3 H, s, OAc), 3.28br (2 H, d, *J* 7 Hz), 5.11br (1 H, t, *J* 7 Hz), 5.67 and 6.75 (1 H each, d, *J* 10 Hz), and 5.98br (1 H, s, H-3) (Found: C, 71.75; H, 6.35. $C_{22}H_{24}O_5$ requires C, 71.7; H, 6.6%).

Acid-catalysed Cyclisation of 6-(3-*Methylbut*-2-*enyl*)*allopteroxylin* (28).—To a solution of (28) (34 mg) in glacial acetic acid (0.5 ml) was added concentrated hydrochloric acid (1 drop). The solution was heated under reflux for 1 h then evaporated almost to dryness *in vacuo*, and the product was isolated by extraction into chloroform. The *chroman* (31) (35 mg), purified by preparative t.l.c. in benzene–acetone (10 : 1), has m.p. 168—170° (from light petroleum), $\nu_{max.}$ 1 650, 1 615, 1 587, and 1 575 cm^{-1}; $\lambda_{max.}$ 223, 265, 295, and 341 nm (ε 19 000, 36 900, 3 900, and 4 600); δ 1.43 and 1.47 (6 H each, s), 1.81 and 2.67 (2 H each, t, *J* 7 Hz), 2.28br (3 H, s), 5.56 and 6.77 (1 H each, d, *J* 10 Hz), and 5.97br (1 H, s, H-11) (Found: C, 73.3; H, 6.7. $C_{20}H_{22}O_4$ requires C, 73.6; H, 6.8%).

Heating a solution of (28) (70 mg) in methanol (10 ml) and concentrated hydrochloric acid (0.4 ml) under reflux for 3 h gave a mixture (*ca.* 1 : 1 by n.m.r.), separated by preparative t.l.c., of the chroman (31) and the product of addition of methanol to the side-chain double bond. This latter compound was not completely characterised, but has δ 1.24 and 1.47 (6 H each, s), *ca.* 1.7 and 2.65 (2 H each, m), 2.35br (3 H, s), 3.28 (3 H, s, OCH_3), 5.55 and 6.68 (1 H each, d, *J* 10 Hz), 6.00br (1 H, s, H-3), and 12.97 (1 H, s, ArOH). Compounds (21) and (23) were unchanged from treatment under these latter conditions.

Hydrogenation of 6-(3-*Methylbut*-2-*enyl*)*allopteroxylin* (28).—Hydrogenation of (28) (40 mg) in ethanol (20 ml) over 10% palladium–charcoal (20 mg) for 1 h gave the tetrahydro-derivative (32), m.p. 117—118° (from methanol–water), δ 0.94 (6 H, d, 5.5 Hz), 1.36 (6 H, s), *ca.* 1.4 (3 H, m), 1.81 and 2.74 (2 H each, t, *J* 6.5 Hz), 2.33br (3 H, s), *ca.* 2.45 (2 H, m), 5.98br (1 H, s, H-3), and 12.69 (1 H, s, ArOH), identical with authentic hexahydrodeoxysorbifolin (32) [1] by spectral and t.l.c. comparison. However, the previously obtained [1] (32), m.p. 96—98°, was found to have traces of an impurity (t.l.c.). The hydrogenation of sorbifolin (1) (257 mg) was repeated and the hexahydrodeoxysorbifolin (32) (88 mg) was isolated by preparative t.l.c. [m.p. 117—118° (from methanol–water)]; it was identical with the material prepared from (28).

Synthesis of 6-(3-*Methylbut*-2-*enyl*)*allopteroxylin* (28).—A solution of allopteroxylin (6) (57 mg) in dry toluene (1 ml) was added dropwise to a suspension of sodium hydride (8 mg) in dry toluene (3 ml). When effervescence ceased, part of the toluene (2 ml) was removed *in vacuo*, and 3-methylbut-2-enyl bromide (40 mg) was added. The mixture was heated under reflux for 20 h, cooled, diluted with chloroform, and washed with aqueous sodium hydrogen carbonate and water. The crude product was separated into unchanged (6) (18 mg) and 6-(3-methylbut-2-enyl)allopteroxylin (28) (16 mg), m.p. 99—101°, identical with the natural product.

Hydrogenation of Anhydrosorbifolin (33).—Hydrogenation of (33) (6 mg) in ethanol (5 ml) over 5% palladium–charcoal (4 mg) for 30 min yielded hexahydrodeoxysorbifolin (32), identical with authentic material.

Dehydration of Sorbifolin (1) *to Anhydrosorbifolin* (33).—Redistilled thionyl chloride (0.5 ml) at 0 °C was added dropwise to a solution of sorbifolin (1) (60 mg) and dry pyridine (0.5 ml) in dry acetone (15 ml) at 0 °C. After 5 min, crushed ice (equivalent to *ca.* 10 ml of water) was added, and the yellow precipitate extracted into chloroform. The crude product (55 mg) was mainly (33) (t.l.c.), and was purified by preparative t.l.c. to yield anhydrosorbifolin (33) (20 mg), identical with the natural product.

Synthesis of Sorbifolin (1).—A solution of 6-(3-methylbut-2-enyl)allopteroxylin acetate (29) (25 mg) and Methylene Blue in methanol (10 ml) was irradiated with a Hanovia medium-pressure mercury vapour lamp (140 W) while oxygen was bubbled through the solution. After 12 h, t.l.c. showed the absence of the starting material and the presence of one new spot. Partial evaporation of solution *in vacuo*, dilution with water, and extraction into chloroform gave the crude hydroperoxide (37), which was immediately reduced by addition of an excess of triphenylphosphine. After 1.5 h, the solution was evaporated and the solvent replaced by methanol saturated with ammonia. After 1 h, hydrolysis of the acetate was complete (t.l.c.) and the crude product was separated to give sorbifolin (1), identical with the natural product.

The Epoxy-methyl Ether (38).—Methylation of (28) (60 mg) with an excess of methyl iodide and dry potassium carbonate in dry acetone under reflux for 6 h gave the *methyl ether*, m.p. 101—102° (from methanol–water), δ 1.48 (6 H, s), 1.68br and 1.82br (3 H each, s), 2.30br (3 H, s), 3·38br (2 H, d, *J* 7 Hz), 3.87 (3 H, s, OCH_3), 5.20br (1 H, t, *J* 7 Hz), 5.63 and 6.73 (1 H each, d, *J* 10 Hz), and 6.00br (1 H, s, H-3) (Found: C, 74.1; H, 7.2. $C_{21}H_{24}O_4$ requires C, 74.1; H, 7.1%). *m*-Chloroperbenzoic acid (40 mg) in dichloromethane (15 ml) at −5 °C was added to the methyl ether (80 mg) in dichloromethane (20 ml) at −5 °C. After 30 min at −5 °C, the solution was washed with sodium sulphite and sodium hydroxide solutions and evaporated. The *epoxy-methyl ether* (38), isolated by preparative t.l.c., has m.p. 116—118.5° (from ethyl acetate–light petroleum), δ 1.29 and 1.44 (3 H each, s), 1.51 (6 H, s), 2.33br (3 H, s), *ca.* 2.97 (3 H, A_2Bm), 3.91 (3 H, s), 5.68 and 6.79 (1 H each, d, *J* 10 Hz), and 6.07br (1 H, s, H-3) (Found: C, 70.8; H, 6.5. $C_{21}H_{24}O_5$ requires C, 70.8; H, 6.8%).

Treatment of the Epoxy-methyl Ether (38) *with Base.*—(*a*) The epoxide (38) (5 mg) in dry toluene (10 ml) and an excess of sodium hydride were heated under reflux for 7 h. The epoxide was unchanged.

(*b*) The epoxide (38) (10 mg) in 1,5-diazabicyclo[4.3.0]non-5-ene (0.5 ml) was heated at 100 °C for 1 h. T.l.c. showed mostly unchanged (38) and a small amount of new material which did not correspond to (2).

Acid-catalysed Cyclisation of Sorbifolin (1) *to Spatheliabischromen* (4).—3N-Sulphuric acid (3 drops) was added to a solution of sorbifolin (1) (200 mg) in acetic acid (10 ml). After 20 min at room temperature, the mixture was diluted with water and extracted with chloroform. Preparative t.l.c. of the crude product gave spatheliabischromen (4) (70 mg), identical with the natural product.

We thank Professor Y. L. Chow for the mass spectra.

[6/785 *Received*, 22*nd April*, 1976]