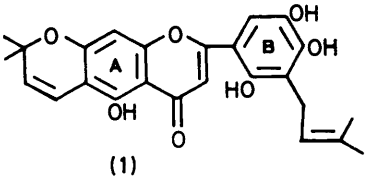
Chemical Investigation of Ceylonese Plants. Part 24.† New Chromenoflavonoids from the bark of *Artocarpus nobilis* Thw. (Moraceae) [1]

By **N. Savitri Kumar, Gowsala Pavanasasivam, M. Uvais S. Sultanbawa,*** and (in part) **Rajeswari Mageswaran,** Department of Chemistry, University of Sri Lanka, Peradeniya Campus, Peradeniya, Sri Lanka

From the bark extract of *Artocarpus nobilis* Thw. (Moraceae) six new chromenoflavonoids have been isolated. Five of them have been characterised and named artobilochromen (1), chromanoartobilochromen *b* (8), (−)-dihydrofuranoartobilochromen *a* (12), (−)-dihydrofuranoartobilochromen b_1 (14), and dihydrofuranoartobilochromen b_2 (13). Artobilochromen (1) with formic acid gave chromanoartobilochromens *a* (7) and *b* (8), and with dichlorodicyanobenzoquinone gave (±)-dihydrofuranoartobilochromen *a* (12).

Artocarpus nobilis Thw. is the only endemic species [2] of the genus *Artocarpus* belonging to the family Moraceae found in Sri Lanka. It is abundant, in wet, low country, up to an elevation of 2 500 ft. The chemistry of the Moraceae has been reviewed,[3] and we have reported [4] on some triterpenoid constituents of the bark of several species of the genus *Artocarpus*. The benzene and methanol extracts of the bark of *Artocarpus nobilis* Thw. have been shown to contain six flavonoids; the structures of five of these have been established in the present study.

T.l.c. showed the presence of five flavonoid compounds in the benzene extract. These were separated and purified by column chromatography over silica gel followed by fractional precipitation. The major compound in the extract (0.8%) has been named artobilochromen (1). Colour tests with iron(III) chloride



(1)

(green) and magnesium–concentrated hydrochloric acid (orange) [5] together with u.v. spectral data (Table 1) indicated that artobilochromen was a flavone. Elemental analysis and mass spectral data (M^+ 436) were in

† Part 23, S. P. Gunasekera and M. U. S. Sultanbawa, *J.C.S. Perkin I*, 1977, 418.

[1] G. Pavanasasivam, M. U. S. Sultanbawa, and R. Mageswaran, *Chem. and Ind.*, 1974, 875.

[2] (*a*) R. Mageswaran, M. U. S. Sultanbawa, and M. M. Manickavasagar, *Proc. Ceylon Assoc. Adv. Sci.*, 1970, **26**, 78; (*b*) G. Pavanasasivam and M. U. S. Sultanbawa, *ibid.*, 1973, **29**, 139.

[3] K. Venkataraman, *Phytochemistry*, 1972, **11**, 1571.

[4] G. Pavanasasivam and M. U. S. Sultanbawa, *Phytochemistry*, 1973, **12**, 2725.

[5] K. Venkataraman in 'The Chemistry of Flavonoid Compounds,' ed. T. A. Geissmann, Pergamon, Oxford, 1962, p. 72.

agreement with the formula $C_{25}H_{24}O_7$. The trimethyl ether (M^+ 478) gave a green colour with alcoholic iron(III) chloride indicating the presence of a chelated hydroxy-group. Acetylation with acetic anhydride–pyridine yielded a tetra-acetate (M^+ 604) which did not respond to the iron(III) chloride test; thus artobilochromen contains four hydroxy-groups. The presence of two ethylenic bonds was shown by the formation of a tetrahydro-derivative (M^+ 440) on hydrogenation.

Information regarding the pattern of hydroxylation was obtained from the following u.v. spectral data.[6a] Addition of aluminium chloride resulted in a bathochromic shift of Band I ($\Delta\lambda$ 80 nm). A hypsochromic shift ($\Delta\lambda$ 55 nm) was observed in Band I on subsequent addition of hydrochloric acid. These observations indicate the presence of a chelated hydroxy-group, most probably at C-5, and two *ortho*-hydroxy-groups. Band II was unaffected by the presence of sodium acetate, thus indicating the absence of a free 7-OH group. Sodium acetate–boric acid shifted Band I to 365 nm ($\Delta\lambda$ 15 nm), confirming the presence of two *ortho*-groups. Sodium methoxide caused a bathochromic shift of Band I, indicating the presence of a free 4′-OH group; subsequent decomposition was probably due to the presence of *ortho*- and/or *para*-hydroxy-groups.[6a] The u.v. spectrum thus showed that the compound was a flavone with a 5-OH, a 4′-OH, and two *ortho*-hydroxy-groups, probably at positions 3′ and 4′ or 4′ and 5′. The relatively low intensity of Band I in the u.v. spectrum of artobilochromen may be attributed to some steric factor which results in the loss of conjugation of ring B with the chromone ring.[6b]

In the n.m.r. spectrum of artobilochromen (1) (Table 2) two vinyl doublets at τ 3.35 and 4.33 (J 10 Hz) together with a signal at τ 8.54 corresponded to the olefinic protons and the methyl groups in a chromen system.[7] Signals at τ 8.41 and 8.54 (methyls) a two-proton doublet (7 Hz) at τ 6.84 (methylene, benzylic and allylic), and a broad one-proton triplet at τ 4.86 indicated the presence of a prenyl unit in the form of a $\gamma\gamma$-dimethylallyl group.[8] The presence of a chromen system and the $\gamma\gamma$-dimethylallyl group were confirmed by the n.m.r. spectrum of the tetrahydro-derivative (see Experimental section). The singlets at τ 3.12, 3.40, and 3.84 were unaffected by hydrogenation. The singlet at τ 3.12 could be assigned to the 3-H of the heterocycle and the one at τ 3.84 to the 8-H of ring A.[9] The remaining singlet at τ 3.40 was probably due to a ring B proton, However difficulties have been encountered previously in the assignments of the signals due to the 3-H of the heterocycle and the protons of a heavily substituted aromatic ring, such as the ring B or artobilochromen.[8]

Mass spectral fragmentation (Table 4) was consistent with the presence of a 2,2-dimethylchromen system: the molecular ion readily lost 15 mass units to give the base peak at m/e 421,[10] and a retro-Diels–Alder process then gave an ion at m/e 203.

In the mass spectrum of compounds having a prenyl chain adjacent to a hydroxy-group, fragmentation occurs with loss of C_4H_6 (56 mass units).[11a] If such a chain is adjacent to a methoxy-group, additional rearrangements

TABLE 1

U.v. spectral data [$\lambda_{max.}$(log$_{10}$ ε)] of the chromenoflavonoids

Solvent/reagents:	MeOH	NaOAc	$AlCl_3$	$AlCl_3$–HCl	NaOAc–H_3BO_3	NaOMe
Artobilochromen (1)	267 (4.63)	265 (4.68)				
	297 (4.13)					
	350 (3.34)	348 (3.35)	430 (3.90)	405 (3.85)	365 (3.34)	360 (3.72)
Artobilochromen monomethyl ether	269 (4.76)					
	300 (4.05)					
	347 (4.00)	347 (3.91)	400 (3.98)	400 (3.90)	348 (3.90)	366 (3.82)
Chromanoartobilochromen *a* (7)	269 (4.45)	269 (4.45)	276 (4.60)	276 (4.54)	270 (4.57)	270 (4.40)
	300 (4.00)					
	340 (3.94)	370 (4.26)	420 (4.07)	400 (3.87)	362 (4.09)	375(4.02)
Chromanoartobilochromen *b* (8)	266 (4.40)	265 (4.50)	275 (4.45)	275 (4.45)	262 (4.46)	270 (4.41)
	300 (3.84)					
	350 (3.85)	347 (3.97)	425 (3.90)	415 (3.83)	345 (3.86)	340 (3.75)
(±)-Dihydrofuranoartobilochromen *a* (12)	261 (4.31)	258 (4.35)	275 (4.31)	280 (4.30)	262 (4.21)	267 (4.29)
	307 (3.99)					
	385 (3.85)	420 (3.82)	450 (3.59)	415 (3.57)	410 (3.81)	430 (3.69)
Dihydrofuranoartobilochromen b_2 (13)	273 (4.40)	267 (4.02)	282 (4.43)	282 (4.43)	274 (3.93)	267 (4.05)
			322 (4.18)	320 (4.17)		
			350 (4.14)	347 (4.10)		
	385 (4.06)	422 (3.76)	430 (4.06)	420 (3.99)	384 (3.57)	430 (3.71)
(−)-Dihydrofuranoartobilochromen b_1 (14)	268 (4.56)	270 (4.48)	282 (4.60)	282 (4.58)	270 (4.45)	275 (4.47)
	365 (3.97)	350 (3.94)	350 (3.95)	347 (3.92)	360 (4.16)	375 (3.94)
			410 (3.64)	410 (3.64)		
Unidentified flavonoid (15)	267 (4.55)	267 (4.55)				
	350 (3.91)	380 (3.90)	405 (3.74)	405 (3.72)	350 (3.83)	410 (3.95)

[6] (*a*) T. J. Mabry in ' Perspectives in Phytochemistry,' eds. J. B. Harborne and T. Swain, Academic Press, London, 1969, pp. 1—43; (*b*) P. Nair, A. V. Rama Rao, and K. Venkataraman, *Beiträge zur Biochemie und Physiologie von Naturstoffen*, 1964, 317.

[7] B. F. Burrows, W. D. Ollis, and L. M. Jackmann, *Proc. Chem. Soc.*, 1960, 177.

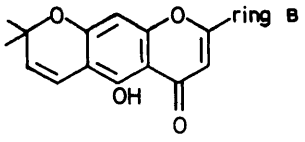
[8] L. M. Jackmann, *Progr. Chem. Org. Natural Products*, 1965, **23**, 315.

[9] T. J. Batterham and R. J. Highet, *Austral. J. Chem.*, 1964, **17**, 428.

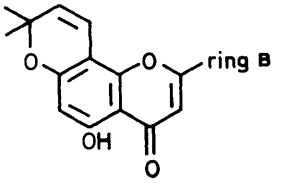
[10] C. S. Barnes and J. Occolowitz, *Austral. J. Chem.*, 1964, **17**, 975.

[11] (*a*) E. Ritchie, W. Taylor, and J. C. Shannon, *Tetrahedron Letters*, 1964, 1437; (*b*) G. H. Stout, M. M. Kran, P. Yates, and H. B. Bhat, *Chem. Comm.*, 1968, 211.

occur with loss of C_3H_7 (43 mass units).[11b] These observations are in general agreement with the mass spectra of artobilochromen (1) and its trimethyl ether. indicating that the prenyl chain is adjacent to a hydroxy-group. Thus the partial structure (2) or (2a) could be assigned.



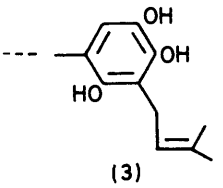
(2)



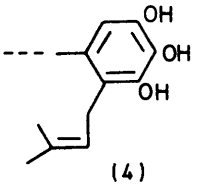
(2a)

The angular position for the chromen ring (2a) was ruled out by a positive response to the Gibbs test,[12] indicating the presence of a free 8-H, and by the effect of acetylation on the chemical shifts of the olefinic α- and β-protons of the chromen. The changes in chemical shift were of the same sign as observed [13] for several 2,2-dimethylchromens in which the OH was in position 5 and therefore *peri* to the α-proton.

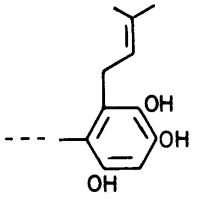
In ring B the positions of the prenyl chain, one proton, and three hydroxy-groups, two of which were *ortho* to each other, had to be determined. One of the three OH groups was in the position 4′, and the mass spectral data signals due to the prenyl chain were replaced by a six-proton singlet at τ 8.66 (chroman CMe_2) and two-proton triplets at τ 7.30 and 8.20 showing that the



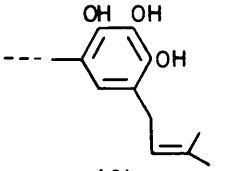
(3)



(4)



(5)



(6)

prenyl chain had cyclised to form a chroman ring. Similarly in the n.m.r. spectrum of (8) the chroman methyl signal appeared at τ 8.94 and those of the methylene protons at τ 7.52 and 8.36. Sodium acetate–boric acid caused a bathochromic shift (Δλ 12 nm) of Band I in the u.v. spectrum of only compound (7), showing that this compound alone had two *ortho*-hydroxy-groups. Hence structures (7) and (8) were assigned to chromanoartobilochromens *a* and *b*, respectively.

This established structure (1) for artobilochromen.*

In the n.m.r. spectrum of artobilochromen (1) the signal at τ 3.40 has been assigned to the 6′-proton. This value is higher than any of the values recorded for this signal in the series of compounds isolated from

TABLE 2

Chemical shifts (τ) in the 100 MHz spectra of artobilochromen (1) and derivatives †

	Chelated OH (1 H)	Chromen Me_2C (6 H)	–CH=CH– (2 H)	3-H [a] (1 H)	8-H (1 H)	6′-H [a] (1 H)	CH_2 (2 H)	–HC= (1 H)	CMe_2 (6 H)	OMe	OAc
(1)	−3.22	8.54	3.35 (d), 4.33 (d) (*J* 10)	3.12	3.84	3.40	6.84 (d, *J* 7)	4.86 (t, *J* 7)	8.41 8.54		
Monomethyl ether	−3.2	8.58	3.41 (d), 4.39 (d) (*J* 10)	3.14	3.87	3.34	6.87 (d, *J* 7)	4.88 (t, *J* 7)	8.44 8.58	6.14 (3 H)	
Trimethyl ether	−3.1	8.58	3.44 (d), 4.39 (d) (*J* 10)	2.95	3.86	3.12	6.95 (d, *J* 7)	4.92 (t, *J* 7)	8.42 8.61	6.08 (3 H) 6.16 (3 H) 6.22 (3 H)	
Tetra-acetate		8.62	3.45 (d), 4.29 (d), (*J* 10)	2.56	3.60	2.77	7.04 (d, *J* 7)	5.04 (t, *J* 7)	8.52 8.71		7.33 (6 H) 7.68 (3 H) 7.80 (3 H)

[a] Assignments tentative.

† The spectra determined for solutions in $[^2H_6]$acetone with tetramethylsilane as internal standard. Unless otherwise indicated all signals are singlets; coupling constants (*J*) are in Hz.

required that the prenyl group be adjacent to a hydroxy-group. Hence four structures (3)—(6) were possible for ring B. Evidence for the partial structure (3) was obtained from cyclisation of artobilochromen with formic acid, which yielded two products, confirming the presence of a prenyl chain flanked by a hydroxy-group on either side. The structures of the two products, which had different R_F values but similar n.m.r. spectra, were established by means of mass spectral (M^+ 436) and n.m.r. data. They have been named chromanoartobilochromens *a* (7) and *b* (8).

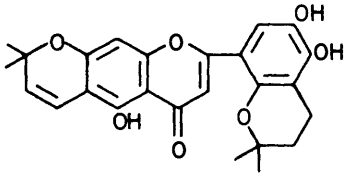
In the n.m.r. spectrum of compound (7) (Table 3)

* Artobilochromen has been shown to be antitumour-active in the NIH, Washington, testing programme.

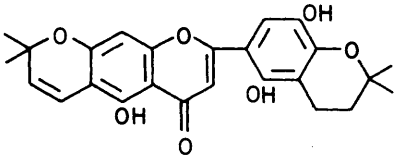
[12] F. E. King, J. T. King, and L. C. Manning, *J. Chem. Soc.*, 1957, 563.

[13] A. Arnone, G. Cardillo, L. Merlini, and R. Mondelli, *Tetrahedron Letters*, 1967, 4201.

Artocarpus by Venkataraman.[14-17] The high chemical shift of the 6'-proton in the chromenoflavonoids isolated from *Artocarpus nobilis* Thw. is attributed to the effect of electron-donating substituents in ring B.[18] For example, the 6'-protons in ferrugone (9) [19a] and in piscerythrone tetramethyl ether (10) [19b] have similar chemical shifts. Likewise in the recently isolated



(7)



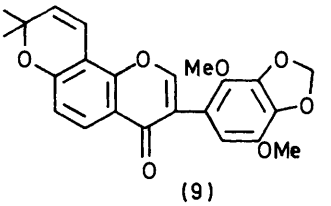
(8)

hermonionic acid (11) and its derivatives, where the pattern of oxygenation is identical with that of ring B in artobilochromen, the aromatic proton signal appeared at τ 3.42—3.72.[20a]

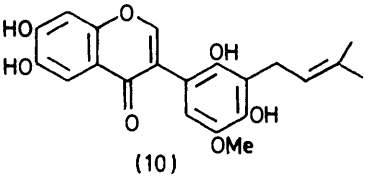
Artobilochromen (1) underwent oxidative cyclisation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to yield one product, which was named dihydrofuranoartobilochromen *a* (12) and was found to be the optically inactive (±)-form of the naturally occurring (−)-dihydrofuranoartobilochromen *a*. Two products might be expected from this reaction, but only one was isolated. In the u.v. spectrum of (12) Band I showed a bathochromic shift ($\Delta\lambda$ 25 nm) with sodium acetate–boric acid, indicating the presence of two *ortho*-hydroxy-groups. Mass spectral data (M^+ 434) and the following n.m.r. data established the structure. The prenyl signals in the n.m.r. spectrum of (1) were replaced by those due to an isopropenyldihydrofuran:[8] the vinylic methyl signal appeared at τ 8.20, the olefinic proton signals were observed at τ 5.34 and 5.66, and the CH and CH_2 signals gave an ABX spectrum.

The structures of the formic acid cyclisation products and that of dihydrofuranoartobilochromen *a* (12) provided additional evidence for the structure of artobilochromen (1).

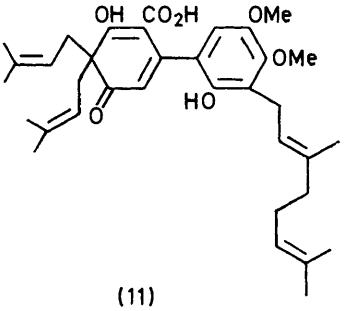
The second compound isolated from the benzene extract of the bark was a dark yellow solid named dihydrofuranoartobilochromen b_2 (13). Colour reactions with iron(III) chloride (green) and magnesium–concentrated hydrochloric acid (orange) indicated that it was a flavone. Elemental analysis and mass spectral data (M^+ 434) agreed with the molecular formula $C_{25}H_{22}O_7$. The dimethyl ether (M^+ 462) gave a green colour with iron(III) chloride, indicating the presence of a chelated hydroxy-group. The triacetate (M^+ 560) gave a negative response to iron(III) chloride, indicating that



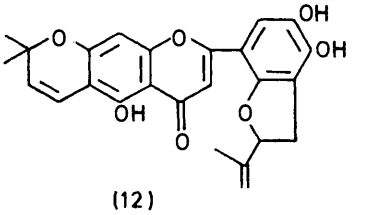
(9)



(10)



(11)



(12)

it was fully acetylated, and that dihydrofuranoartobilochromen b_2 contained three hydroxy-groups.

In the u.v. spectrum of dihydrofuranoartobilochromen b_2 (Table 1), addition of aluminium chloride caused a bathochromic shift of Band I ($\Delta\lambda$ 45 nm) which was

[14] P. C. Parthasarathy, P. V. Radhakrishnan, S. S. Rathi, and K. Venkataraman, *Indian J. Chem.*, 1969, **7**, 101.
[15] A. V. Rama Rao, M. Varadan, and K. Venkataraman, *Indian J. Chem.*, (*a*) 1971, **9**, 7; (*b*) 1973, **11**, 298.
[16] V. Radhakrishnan, A. V. Ram Rao, and K. Venkataraman, *Tetrahedron Letters*, 1965, 663.
[17] V. H. Deshpande, P. C. Parthasarathy, and K. Venkataraman, *Tetrahedron Letters*, 1968, 1715.
[18] J. A. Pople, W. G. Schneider, and H. J. Bernstein in 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 258.
[19] (*a*) R. J. Highet and P. F. Highet, *J. Org. Chem.*, 1967, **32**, 1055; (*b*) C. P. Falshaw, W. D. Ollis, J. A. Moore, and K. Magnus, *Tetrahedron*, 1966, Suppl. 7, 333.
[20] (*a*) S. P. Gunasekera, V. Kumar, and M. U. S. Sultanbawa, unpublished results; (*b*) J. B. Harborne, 'Comparative Biochemistry of the Flavonoids,' Academic Press, New York, 1967.

TABLE 3

Chemical shifts (τ) in the 100 MHz n.m.r. spectra † of the chromenoflavonoids from *Artocarpus nobilis* Thw.

	Chelated OH (1 H)	Chromen CMe_2 (6 H)	-CH=CH- (2 H)	3-H [a] (1 H)	8-H (1 H)	6'-H [a] (1 H)	CMe_2 (2 × 3 H)	O·Me_2C·CH_2·CH_2Ar: Me_2C (6 H)	CH_2 (2 H)	CH_2 (2 H)	OMe (2 × 3 H)	Vinylic Me (3 H)	Vinylic H (2 H)	CH_AH_B·CH_X of dihydrofuran: H_X	H_B	H_A	OAc (3 × 3 H)
Chromanoartobilochromen *a* (7) ($CDCl_3$)	−3.02	8.56	3.42 (d), 4.53 (d) (*J* 10)	2.92	3.76	3.37		8.66	8.20 (m)	7.30 (m)							
triacetate ($CDCl_3$)		8.56	3.35 (d), 4.41 (d) (*J* 10)	2.62	3.56	3.06		8.66	8.25 (m)	7.40 (m)							7.58, 7.71, 7.71
Chromanoartobilochromen *b* (8) [$(CD_3)_2CO$]	−3.22	8.54	3.39 (d), 4.35 (d) (*J* 10)	3.10	3.86	3.41		8.90	8.30 (m)	7.50 (m)							
triacetate [$(CD_3)_2CO$]		8.58	3.41 (d), 4.23 (d) (*J* 10)	2.42	3.54	2.70		8.99	8.24	7.40 (m)							7.72, 7.72, 7.74
(−)-Dihydrofuranoartobilochromen *a* (12) [$(CD_3)_2CO$]	−3.32	8.52 8.54	3.07 (d), 4.33 (d) (*J* 10)		3.88	3.40						8.20	5.34, 5.36	6.00 (d, *J* 8)	6.56 (d, *J* 16)	7.56 (dd, *J* 8, 16)	
triacetate [$(CD_3)_2CO$]		8.48 8.50	3.03 (d), 4.03 (d) (*J* 10)	2.78	3.49	2.03						8.28	5.30, 5.70	6.15 (d), *J* 6)	6.60 (d, *J* 16)	7.51 (dd, *J* 6, 16	
Dihydrofuranoartobilochromen b_2 (13) (C_5D_5N)	−4.0	8.60	2.64 (d), 4.48 (d) (*J* 10)	3.12	3.52	3.46	8.44 8.70			6.52 (dd, *J* 6)							
dimethyl ether ($CDCl_3$)	−3.10	8.52 8.54	3.17 (d), 4.43 (d) (*J* 10)		3.76	3.64	8.32 8.64			6.70	6.04, 6.07						7.69, 7.69, 7.72
(−)-Dihydrofuranoartobilochromen b_1 (14) ($CDCl_3$)	−3.30	8.54 8.56	2.98 (d), 4.39 (d) (*J* 10)		3.86	3.76						8.14	6.36 (d, *J* 8)	6.88 (d, *J* 16)	7.66 (dd, *J* 8, 16)		

[a] Assignments tentative.

† Spectra determined with tetramethylsilane as internal standard; unless otherwise indicated, all signals are singlets; coupling constants (*J*) are given in Hz.

unaffected by the addition of hydrochloric acid. This indicated the absence of *ortho*-hydroxy-groups and the presence of a hydroxy-group at C-5.[6a] Sodium acetate–boric acid has no effect on Band I, thus confirming the absence of *ortho*-hydroxy-groups. Sodium acetate did not affect Band II, indicating the absence of a free 7-OH. Sodium methoxide caused a bathochromic shift of Band I ($\Delta\lambda$ 45 nm) but with decreased intensity revealing the absence of a free 4'-OH group.

In the n.m.r. spectrum of (13) (Table 3) two vinyl proton doublets at τ 2.64 and 4.48 (J 10 Hz) together with a singlet at τ 8.60 suggested the presence of a 2,2-dimethylchromen system as in artobilochromen (1).[7] Signals due to the isopentenyl side chain were absent but instead there were two singlets due to vinylic methyl groups (τ 8.44 and 8.70) and two one-proton doublets at τ 6.50 and 6.56 (J 16 Hz). This suggested the formation of an isopropylidenedihydrofuran ring by oxidative cyclisation with a hydroxy-group. In addition there were three one-proton singlets at τ 3.12, 3.46, and 3.56. That at τ 3.12 was assigned to 3-H of the heterocycle and that at τ 3.52 to 8-H of ring A.[9] The singlet at τ 3.46 was therefore due to a proton in ring B.

TABLE 4

Mass spectral ions from the chromenoflavonoids [a]

Artobilochromen (1)	*m/e*	436 (33)	421 (100)	403 (11)	393 (30)	379 (5)	219 (5)	203 (66)	175 (5)	163 (5)
Chromanoartobilochromen *a* (7)	*m/e*	436 (50)	421 (100)		393 (25)	379 (10)	219 (5)	203 (25)		
Chromanoartobilochromen *b* (8)	*m/e*	436 (53)	421 (100)	408 (1)	393 (22)	381 (7)	219 (1)	203 (34)	175 (2)	
(−)-Dihydrofuranoartobilochromen *a* (12)	*m/e*	434 (40)	419 (100)		393 (4)	380 (3)		203 (4)	165 (1)	149 (3)
Dihydrofuranoartobilochromen b_2 (13)	*m/e*	434 (48)	419 (100)	406 (25)	393 (23)		219 (5)	217 (4)	203 (8)	
(−)-Dihydrofuranoartobilochromen b_1 (14)	*m/e*	434 (100)	419 (50)	403 (20)	289 (25)		219 (5)	217 (3)	203 (15)	
Unidentified compound	*m/e*	436 (4.5)	421 (4)			380 (4)	219 (7)		203 (12)	149 (100)

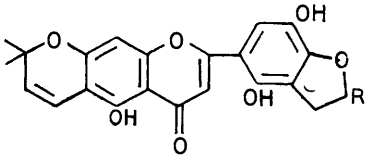
[a] Relative abundances in parentheses.

Mass spectral evidence (Table 4) was consistent with the presence of 2,2-dimethylchromen system and indicated the partial structure (2) as in artobilochromen. The molecular formula showed the presence of seven oxygen atoms. According to partial structure (2) four of the oxygen atoms are contained in rings A and C. The three remaining must therefore be in ring B. Since the compound possessed only three hydroxy-groups, including 5-OH, only two hydroxy-groups could be present in ring B. This was further supported by the formation of a dimethyl ether with diazomethane. The third oxygen atom was probably part of a ring. Since the u.v. spectrum showed the absence of a free 4'-OH, it was possible that an oxygen atom at C-4' was involved in a ring. Hence structure (13) was assigned to dihydrofuranoatrobilochromen b_2. It was optically inactive, in keeping with the assigned structure.

The third compound isolated from the bark extract was a dark yellow solid. It gave an olive-green colour with iron(III) chloride and an orange colour with magnesium–concentrated hydrochloric acid, indicating that it was a flavone.[5] Mass spectral evidence (M^+ 434) and elemental analysis agreed with the formula $C_{25}H_{22}O_7$. The formation of a triacetate (M^+ 560), which gave a negative response to iron(III) chloride, indicated the presence of three hydroxy-groups.

In the u.v. spectrum aluminium chloride caused a bathochromic shift of Band I to 450 nm (Table 1). Subsequent addition of hydrochloric acid produced a hypsochromic shift to 415 nm. This indicated the presence of two *ortho*-hydroxy-groups, and a hydroxy-group most probably at C-5.[6a] The presence of two *ortho*-hydroxy-groups was confirmed by the bathochromic shift of Band I ($\Delta\lambda$ 25 nm) by sodium acetate–boric acid. Sodium acetate did not affect the position of Band II, indicating the absence of a free 7-OH. Sodium methoxide caused a bathochromic shift of Band I ($\Delta\lambda$ 45 nm), showing the presence of a free 4'-OH, but the solution was unstable, probably owing to the presence of the *ortho*-hydroxy-groups.[6a]

I.r., n.m.r., and mass spectral evidence confirmed that



(13) R = =

(14) R = —

this compound was identical with the product of cyclisation of artobilochromen with DDQ. However the natural compound is optically active, $[\alpha]_D^{27}$ −33° (in MeOH), *i.e.* it is (−)-dihydrofuranoartobilochromen *a* (12).

The fourth compound isolated, a pale yellow solid, was named dihydrofuranoartobilochromen b_1 (14). The colourations observed with iron(III) chloride (green) and magnesium–concentrated hydrochloric acid (orange) indicated that it was a flavone. Elemental analysis and mass spectral data (M^+ 434) agreed with the formula $C_{25}H_{22}O_7$. The formation of a triacetate, which did not give a colouration with iron(III) chloride, indicated the presence of three hydroxy-groups.

The n.m.r. spectrum (Table 3) showed a strong resemblance to that of compound (12): signals due to a 2,2-dimethylchromen ring, an isopropenyldihydrofuran ring [as in (12)] and two aromatic protons were observed. The 3-H signal was not located; it was overlapped by the H_α signal of the chromen ring.

U.v. spectral evidence distinguished between dihydrofuranoartobilochromen *a* (12) and dihydrofuranoartobilochromen b_1 (14). The effects of aluminium chloride with and without hydrochloric acid and of sodium methoxide indicated the absence of *ortho*-hydroxy-groups, the presence of a 5-OH and the absence of a free 4′-OH in the latter (Table 1). The absence of a free 4′-OH and the n.m.r. spectral evidence suggested the presence of an isopropenyldihydrofuran ring, formed by oxidative cyclisation of the prenyl chain with the 4′-OH group. Hence dihydrofuranoartobilochromen b_1 was assigned structure (14). The natural product is the (—)-form, $[\alpha]_D^{27}$ —19° (in MeOH).

Work on a fifth flavonoid compound (15) isolated after dihydrofuranoartobilochromen b_1 (14) [1] is in progress.

The methanol extract of the bark yielded a sixth flavonoid compound in addition to the five flavonoid compounds isolated from the benzene extract. This compound was identical with chromanoartobilochromen (8) obtained from the formic acid cyclisation of artobilochromen (mixed m.p. and u.v., i.r., and n.m.r. spectra).

The main components of the bark of *Artocarpus nobilis* Thw. were the chromenoflavonoids. Of the five chromenoflavonoids isolated, artobilochromen was present in large amounts, and may well be the precursor of the others, which could be formed by either additive or oxidative cyclisation. A most unusual feature was the 2′,4′,5′-pattern of oxygenation common to all five compounds. Although a number of isoflavones having this pattern of oxygenation are known,[21] few such flavones are reported (*e.g.* oxyayanin-A,[20b] cycloheterophyllin,[15a] and isocycloheterophyllin,[15b] of which the latter two were isolated from the bark of *Artocarpus heterophyllus* Lam). The other flavonoids isolated thus far from *Artocarpus* have the 2′,4′-pattern of oxygenation; it is likely that the additional hydroxylation on ring B occurs during the final step of the biosynthesis.

Other noteworthy features in the chromenoflavonoids isolated from this plant include (i) the presence of a 2,2-dimethylchroman system, (ii) the presence of ring systems formed as a result of both additive and oxidative cyclisations in the same compound, *e.g.* (8), (iii) the presence of both chromen and dihydrofuran rings in the same compound, *e.g.* (12), (iv) the occurrence of both additive and oxidative cyclisation products in the same plant, and (v) the presence of an isopentenyl side chain on ring B.

EXPERIMENTAL

Analytical thin-layer plates were made with silica gel G (Merck). All R_F values were recorded on plates of thickness 0.25 mm. Merck silica gel (30—70 mesh) was used for column chromatography. M.p.s were determined with a Kofler hot-stage apparatus. Optical rotations were determined with a Bellingham and Stanley polarimeter for solutions in methanol. Microanalyses were carried out by the CSIRO Microanalytical Service, Melbourne, Australia. N.m.r. and mass spectral data were obtained from the Universities of Aberdeen, Sheffield, Strathclyde, and Maryland, and the Australian National University (Canberra). I.r. spectra were recorded with a Perkin-Elmer 257 grating spectrophotometer, and u.v. spectra with a Unicam SP 8000 spectrophotometer.

All acetylations were carried out with acetic anhydride–pyridine. The product was isolated by dilution with water and extraction with ether. The ethereal layer was washed with 2N-hydrochloric acid and water, and dried over anhydrous sodium sulphate.

The bark was collected from Peradeniya. It was chipped, dried, and powdered in a mill. The powdered bark was successively extracted with hot light petroleum (b.p. 60—80 °C), hot benzene, and hot methanol. The benzene extract on evaporation yielded a yellowish brown solid (90 g, 1.6%). The methanol extract on concentration yielded a solid (200 g, 3.6%), and the mother liquor on evaporation afforded a brown solid (35 g, 0.64%). Yields are expressed as a percentage of the dry weight of the plant material used.

Benzene Extract of the Bark.—T.l.c. of the benzene extract in light petroleum–diethyl ether (1 : 5) revealed that it was a mixture. A portion (5 g) was chromatographed over silica gel (125 g); elution with light petroleum–diethyl ether (1 : 1) afforded a bright yellow solid (3 g) (mixture A), found to be a mixture of compounds (1) and (13). Elution with light petroleum–diethyl ether (1 : 3) yielded another yellow solid, shown to be a mixture of compounds (12) and (14) (0.5 g) (mixture B). Further elution with diethyl ether yielded another mixture of flavonoids containing compounds (14) and (15) (1.0 g) (mixture C).

Isolation of Artobilochromen (1) {*5-Hydroxy-8,8-dimethyl-2-[2,4,5-trihydroxy-3-(3-methylbut-2-enyl)phenyl]-8H-benzo-[1,2-b:5,4-b′]dipyran-4-one*} *from Mixture A.* The mixture A (3 g) was chromatographed over silica gel (100 g). Elution of the column with methylene chloride yielded a bright yellow solid (2 g, 0.8%) which was recrystallised from light petroleum–diethyl ether (1 : 1) to give *artobilochromen* (1) as bright yellow crystals, m.p. 244°, R_F 0.75 (from acetone–benzene, 2 : 3); an alcoholic solution slowly turned pink (Found: C, 68.6; H, 5.55%; M^+, 436.152 4. $C_{25}H_{24}O_7$ requires C, 68.8; H, 5.5%; *M*, 436.152 2); $\nu_{max.}$ (KBr) 3 440, 2 990, 2 930, 1 665, 1 640, 1 610, 1 590, 1 570, 1 530, 1 485, 1 465, 1 430, 1 375, 1 360, 1 295, 1 240, 1 185, 1 160, 1 115, 1 080, 975, 920, 880, 845, 835, 805, 775, and 705 cm^{-1}; for u.v., n.m.r., and mass spectral data see Tables. Acetylation of (1) (0.10 g) and recrystallisation of the product from methanol yielded off-white rod-shaped crystals of the *tetra-acetate* (0.065 g), m.p. 184—185° (Found: M^+, 604.193 8. $C_{33}H_{32}O_{11}$ requires *M*, 604.194 4); $\nu_{max.}$ (KBr) 1 775 and 1 660 cm^{-1}; *m/e* 604(30%), 562(33), 547(100), 519(20), 505(20), 477(15), 219(7), and 203(50); for n.m.r. data see Table 2.

Compound (1) (0.05 g) in diethyl ether (10 ml) was treated with ethereal diazomethane for 5 h. Evaporation, and recrystallisation of the residue from methanol yielded the monomethyl ether as pale yellow crystals, m.p. 205—206°,

[21] W. D. Ollis, ' Recent Advances in Phytochemistry,' North Holland, Amsterdam, 1968, p. 329.

giving an olive-green colour with $FeCl_3$; M^+ 450; $\nu_{max.}$ (KBr) 3 405, 2 975, 1 655, and 1 560 cm^{-1}; *m/e* 450(55%), 435(100), 417(6), 407(22), 393(7), 219(5), 203(44), and 189(10); for u.v. and n.m.r. data see Tables.

Compound (1) (0.05 g) in methanol (5 ml) was treated with excess of ethereal diazomethane and left overnight. Evaporation and column chromatography afforded the trimethyl ether (0.027 g). Recrystallisation from methanol gave yellow rod-shaped crystals, m.p. 124—125°, giving a green colour with $FeCl_3$; M^+ 478; $\nu_{max.}$ (KBr) 3 440, 2 970, 2 930, 1 650, and 1 620 cm^{-1}; *m/e* 478(33%), 463(100), 445(20), 435(33), 204(7), and 203(30), for n.m.r. data see Table 2.

Compound (1) (0.10 g) in 95% ethanol (50 ml) was hydrogenated over palladium–charcoal. Filtration, evaporation, and recrystallisation of the residue from methanol yielded tetrahydroartobilochromen as pale yellow crystals, m.p. 145°, M^+ 440; $\nu_{max.}$ (Nujol) 3 300 and 1 650 cm^{-1}; $\lambda_{max.}$ (EtOH) 265 (log ε 4.55), 300(4.14), and 360 nm (4.12); τ[$(CD_3)_2CO$; 100 MHz] — 3.1 (1 H, s, chelated OH), 3.08 (1 H, s, 3-H), 3.40 (1 H, s, 6′-H), 3.90 (1 H, s, 8-H), 7.30 (2 H, t, *J* 6.5 Hz pyran CH_2Ar), 7.45 (2 H, m, CH_2Ar), 8.15 (1 H, m, $CHMe_2$), 8.4—8.60 (4 H, complex m, 2 × CH_2·CH_2-Ar), 8.66 (2 × 3 H, s, pyran Me_2), and 9.22 (2 × 3 H, d, *J* 7 Hz $CHMe_2$); *m/e* 440(70%), 423(100), 395(55), 384(85), 369(15), 341(30), 220(6), 205(6), 203(15), and 165(70).

Cyclisation of Artobilochromen with Formic Acid. Artobilochromen (0.50 g) was treated with formic acid (25 ml) and warmed on a water-bath for 15 min. The bright red solution was diluted with water and extracted with ethyl acetate; the extract was refluxed with animal charcoal, filtered, and evaporated. T.l.c. revealed three spots.

(i) *Chromanoartobilochromen* a (7) {2-(5,6-*dihydroxy*-2,2-*dimethylchroman*-8-*yl*)-5-*hydroxy*-8,8-*dimethyl*-8H-*benzo*-[1,2-b:5,4-b′]*dipyran*-4-*one*}. The residue was chromatographed on a column. Elution with chloroform afforded a yellow solid (0.10 g). This was dissolved in the minimum amount of chloroform and light petroleum was added dropwise till the compound was precipitated. Filtration yielded chromanoartobilochromen *a* (7) as a yellow solid, m.p. 155°, R_F 0.85 (acetone–benzene, 2 : 3), giving an olive-green colour with $FeCl_3$; M^+ 436; $\nu_{max.}$ (Nujol) 3 420, 1 650, 1 570, 1 450, 1 370, 1 280, 1 150, 1 110, 1 005, 950, 885, 830, 765, and 720 cm^{-1}; for u.v., n.m.r., and mass spectral data see Tables. Acetylation of artobilochromen *a* (0.05 g) and recrystallisation of the product from diethyl ether–light petroleum (1 : 2) gave *the triacetate* (0.03 g), m.p. 169—170°, showing a negative reaction with $FeCl_3$ (Found: M^+, 562.183 7. $C_{31}H_{30}O_{10}$ requires *M*, 562.183 9); $\nu_{max.}$ (Nujol) 1 760, 1 620, and 1 570 cm^{-1}; *m/e* 562(15%), 547(2), 520(75), 505(100), 478(15), 436(15), 421(5), 405(10), 219(5), 203(15), and 149(10); for u.v. and n.m.r. data see Tables.

(ii) *Chromanoartobilochromen* b (8) {2-(5,8-*dihydroxy*-2,2-*dimethylchroman*-6-*yl*)-5-*hydroxy*-8,8-*dimethyl*-8H-*benzo*-[1,2-b:5,4-b′]*dipyran*-4-*one*}. Elution of the column with chloroform–methanol (98 : 2) yielded unchanged artobilochromen (0.25 g). Chloroform–methanol (95 : 5) then eluted chromanoartobilochromen *b* (8) (0.075 g), which was purified by dissolving in the minimum amount of ethyl acetate and precipitating by dropwise addition of chloroform; m.p. 148°; R_F 0.35 (acetone–benzene, 2 : 3); olive-green colour with $FeCl_3$; M^+ 436; $\nu_{max.}$ (Nujol) 3 300, 1 645, 1 490, 1 370, 1 365, 1 275, 1 150, 1 105, 965, 830, and 720 cm^{-1}; $\lambda_{max.}$ (MeOH) 266 (log ε 4.42), 300(3.90), and 350 (3.87); $\lambda_{max.}$ (MeOH–$AlCl_3$) 275 (log ε 4.45) and 415(3.94); $\lambda_{max.}$ (MeOH–$AlCl_3$–HCl) 275 (log ε 4.46) and 405(3.92); $\lambda_{max.}$ (MeOH–NaOMe) 270 (log ε 4.45) and 340 nm (3.69); τ[$(CD_3)_2CO$; 100 MHz] —3.22 (1 H, s, chelated OH), 3.14 (1 H, s, 3-H), 3.43 (1 H, d, *J* 10 Hz, chromen =C*H*Ar), 3.46 (1 H, s, 6′-H), 3.90 (1 H, s, 8-H), 4.39 (1 H, d, *J* 10 Hz, chromen Me_2CCH=), 7.52 (2 H, m, $ArCH_2$), 8.36 (2 H, m, CH_2·CMe_2), 8.60 (6 H, s, chromen CMe_2), and 8.94 (6 H, s, chroman CMe_2); *m/e* 436(53%), 421(100), 408(0.3), 393(22), 381(6.3), 219(0.5), 203(33.5), and 175(1.5).

Cyclisation of Artobilochromen with DDQ; Isolation of Dihydrofuranoartobilochromen a (12) {2-(2,3-*Dihydro*-4,5-*dihydroxy*-2-*isopropenylbenzofuran*-7-*yl*)-5-*hydroxy*-8,8-*dimethyl*-8H-*benzo*[1,2-b:5,4-b′]*dipyran*-4-*one*}.—Artobilochromen (0.10 g) was refluxed with DDQ (0.10 g) in dry benzene (50 ml) for 1 h. The mixture was cooled and then filtered and evaporated to a dark brown residue. Column chromatography over silica gel and elution with chloroform yielded (±)-*dihydrofuranoartobilochromen* a (12) as a yellow solid (0.02 g). Fractional precipitation by using chloroform and light petroleum yielded yellow crystals, m.p. 148°, R_F 0.60 (acetone–benzene, 2 : 3); olive-green colour with $FeCl_3$; M^+ 434; $\nu_{max.}$ (Nujol) 3 400, 1 640, 1 450, 1 370, 1 280, 1 150, 1 105, 960, 830, 760, and 720 cm^{-1}; $\lambda_{max.}$ (MeOH) 261 (log ε 4.31), 307(3.99), and 385(3.85); $\lambda_{max.}$ (MeOH–$AlCl_3$) 275 (log ε 4.31), 350(3.88), and 450(3.59); $\lambda_{max.}$ (MeOH–$AlCl_3$–HCl) 280 (log ε 4.30), 370(3.88), and 415(3.57); $\lambda_{max.}$ (MeOH–NaOAc) 258(4.35) and 420(3.82); $\lambda_{max.}$ (MeOH–NaOAc–H_3BO_3) 262 (log ε 4.21) and 410(3.81); $\lambda_{max.}$ (MeOH–NaOMe) 267 (log ε 4.29), 345(3.88), and 430 nm (3.59); τ[$(CD_3)_2SO$; 100 MHz] —3.32 (1 H, s, chelated OH), 3.15 (1 H, d, *J* 10 Hz, chromen =C*H*Ar), 3.52 (1 H, s, 6′-H), 3.84 (1 H, s, 8-H), 4.30 (1 H, d, *J* 10 Hz, chromen Me_2CCH=), 5.38 and 5.84 (2 × 1 H, s, olefinic protons) (the signals due to the dihydrofuran ring were obscured by the solvent), 8.28 (3 H, s, vinylic CH_3), and 8.55 and 8.58 (2 × 3 H, s, chromen CMe_2), *m/e* 434(27%), 419(100), 403(2), 293(4), 391(4), 380(4), 337(3), 203(5), 165(2), and 149(3).

Isolation of Dihydrofuranoartobilochromen b_2 (13) {2-(2,3-*Dihydro*-4,7-*dihydroxy*-2-*isopropylidenebenzofuran*-5-*yl*)-5-*hydroxy*-8,8-*dimethyl*-8H-*benzo*[1,2-b:5,4-b′]*dipyran*-4-*one*}. —After artobilochromen was obtained from mixture A the column was eluted with methylene chloride–methanol (95 : 5) to yield another yellow solid (0.20 g, 0.07%), which was purified by fractional precipitation with chloroform–light petroleum. *Dihydrofuranoartobilochromen* b_2 was obtained as a yellow solid, m.p. 135°, R_F 0.85 (acetone–benzene, 2 : 3), $[\alpha]_D^{27}$ 0° (Found: C, 69.3; H, 5.0%; M^+, 434. $C_{25}H_{22}O_7$ requires C, 69.1; H, 5.1%; *M*, 434); $\nu_{max.}$ (Nujol) 3 300, 1 655, 1 615, 1 555, 1 470, 1 380, 1 370, 1 270, 1 250, 1 210, 1 188, 1 160, 1 120, 1 095, 980, 965, 885, 845, 815, 760, and 740 cm^{-1}; for u.v., n.m.r., and mass spectral data see Tables. Acetylation of dihydrofuranoartobilochromen b_2 (0.05 g) and recrystallisation of the product from diethyl ether–light petroleum (1 : 1) afforded the *triacetate* as pale yellow crystals, m.p. 275—277°; negative reaction with $FeCl_3$ (Found: M^+, 560.167 8. $C_{31}H_{28}O_{10}$ requires *M*, 560.168 2); $\nu_{max.}$ (Nujol) 1 760 and 1 615 cm^{-1}; *m/e* 560(10%), 518(50), 503(100), 476(20), 461(50), 434(20), 419(40), 216(7), and 203(10). N.m.r. data were not obtained owing to insolubility.

Dihydrofuranoartobilochromen b_2 (0.05 g) in methanol (5 ml) was treated with an excess of ethereal diazomethane and left overnight. Evaporation and recrystallisation from

methanol yielded the dimethyl ether (0.03 g) as pale yellow needles, m.p. 251°, giving a green colouration with $FeCl_3$; M^+ 462; $\nu_{max.}$ (Nujol) 1 670 and 1 560 cm^{-1}; for n.m.r. data see Table 3.

Isolation of (−)-*Dihydrofuranoartobilochromen* a (12). {2-(2,3-*Dihydro*-4,5-*dihydroxy*-2-*isopropenylbenzofuran*-7-*yl*)-5-*hydroxy*-8,8-*dimethyl*-8H-*benzo*[1,2-b:5,4-b′]*dipyran*-4-*one*} *from Mixture B*.—Mixture B (0.5 g) was subjected to column chromatography over silica gel. Elution with light petroleum–diethyl ether (1 : 1) gave a dark yellow solid (0.30 g, 0.10%) which was purified by fractional precipitation from chloroform–light petroleum. (−)-*Dihydrofuranoartobilochromen* a was obtained as yellow solid, m.p. 146—147°, $[\alpha]_D^{27}$ −33°, R_F 0.60 (acetone–benzene, 2 : 3), giving an olive-green colour with $FeCl_3$ and an orange colour with Mg–conc. HCl (Found: C, 69.25; H, 5.05%; M^+, 434. $C_{25}H_{22}O_7$ requires C, 69.1; H, 5.05%; M, 434); $\nu_{max.}$ (Nujol) 3 400, 1 640, 1 450, 1 370, 1 280, 1 150, 1 105, 960, 830, 760, and 720 cm^{-1}; for n.m.r. and mass spectral data see Tables. Acetylation of (−)-dihydrofuranoartobilochromen *a* (0.05 g) and recrystallisation of the product from diethyl ether–light petroleum (1 : 2) yielded the *triacetate* as a pale yellow solid (0.03 g), m.p. 194—195° (Found: M^+, 560.168 9. $C_{31}H_{28}O_{10}$ requires M, 460.168 2); *m/e* 560(26%), 545(60), 518(22), 509(30), 456(20), 434(28), 419(15), 203(70), and 149(100); for n.m.r. data see Table 3.

Isolation of (−)-*Dihydrofuranoartobilochromen* b_1 (14) {2-(2,3-*Dihydro*-4,7-*dihydroxy*-2-*isopropenylbenzofuran*-5-*yl*)-5-*hydroxy*-8,8-*dimethyl*-8H-*benzo*[2,3-b:5,4-b′]*dipyran*-4-*one*} *from Mixture C*.—Mixture C (1.0 g) was chromatographed over silica gel (50 g). Elution with chloroform–methanol (95 : 5) gave a yellow solid (0.30 g, 0.10%), which was recrystallised from light petroleum to yield (−)-*dihydrofuranoartobilochromen* b_1 (14) as a pale yellow amorphous solid, m.p. 149°, R_F 0.15 (acetone–benzene, 2 : 3), $[\alpha]_D^{27}$ −19°, giving an olive-green colour with $FeCl_3$ and an orange colour with Mg–conc. HCl (Found: C, 69.2; H, 5.05%; M^+, 434. $C_{25}H_{22}O_7$ requires C, 69.1; H, 5.1%; M, 434); $\nu_{max.}$ (Nujol) 3 400, 1 650, 1 575, 1 450, 1 370, 1 270, 1 225, 1 150, 1 100, 1 070, 960, 890, and 720 cm^{-1}; for u.v., n.m.r., and mass spectral data see Tables. Acetylation of dihydrofuranoartobilochromen b_1 (0.05 g) and recrystallisation from diethyl ether–light petroleum (1 : 1) gave *the triacetate* as a pale yellow crystalline solid, m.p. 161° (Found: M^+, 560.167 8. $C_{31}H_{28}O_{10}$ requires M, 560.168 2); *m/e* 560 (37%), 545(50), 524(43), 518(12), 509(45), 503(30), 456(25), 451(50), 434(25), 419(25), 220(30), 203(62), and 149(100).

Isolation of an Unidentified Compound (15) *from Mixture C*.—Further elution of the column with chloroform–methanol (85 : 15) furnished crude compound (15) as a brown solid (0.50 g, 0.17%). It was dissolved in ethyl acetate and light petroleum was added dropwise until impurities were precipitated. The filtrate was concentrated and more light petroleum was added to precipitate compound (15) as a pale yellow solid, m.p. 298° (decomp.), R_F 0.45 (acetone–benzene, 2 : 3), giving an olive-green colour with $FeCl_3$ and a dark yellow colour with Mg–conc. HCl (Found: C, 68.6; H, 5.35%; M^+, 436. Calc. for $C_{25}H_{24}O_7$: C, 68.8; H, 5.5%; M, 436); $\nu_{max.}$ (Nujol) 3 400, 1 650, 1 580, 1 440, 1 370, 1 270, 1 150, 1 105, 1 070, 960, 880, 830, 760, and 720 cm^{-1}; for u.v. and mass spectral data see Tables.

Compound (15) (0.05 g) was treated with pyridine (5 ml) and acetic anhydride (5 ml) and left overnight. The usual work-up gave a tetra-acetate, m.p. 244—245°, giving a negative reaction with $FeCl_3$; M^+ 604; *m/e* 604(15%), 576(12), 562(35), 547(55), 520(35), 505(50), 503(62), 478(25), 435(35), 419(55), 379(50), 219(31), and 203(100).

Methanol Extract of the Bark.—The solid obtained from the methanol extract (200 g, 3.6%) had the same t.l.c. pattern as the benzene extract. The mother liquor (35 g, 0.64%) contained another flavonoid in addition to the flavonoids isolated from the benzene extract.

Isolation of Chromanoartobilochromen b (8).—A portion of the mother liquor from the methanol extract (5 g) was dissolved in the minimum quantity of ethanol and added dropwise with stirring to an excess of water. The insoluble solid was filtered off and found to consist mainly of the flavonoids (1) and (12)—(15). The filtrate was extracted with ethyl acetate. Evaporation left a dark yellow residue (0.15 g, 0.02%), which was mainly chromanoartobilochromen *b*. It was dissolved in a small amount of ethyl acetate and light petroleum was added until impurities were precipitated. The filtrate was concentrated, a small amount of chloroform was added, and light petroleum was added dropwise until *chromanoartobilochromen* b (8), was precipitated as a bright yellow solid, m.p. 150°, R_F 0.35 (acetone–benzene, 2 : 3), giving an olive-green colour with $FeCl_3$ and an orange colour with Mg–conc. HCl (Found: C, 68.9; H, 5.5%; M^+, 436. $C_{25}H_{24}O_7$ requires C, 68.8; H, 5.5%; M, 436); $\nu_{max.}$ (Nujol) 3 300, 1 645, 1 490, 1 370, 1 365, 1 275, 1 150, 1 105, 965, 830, and 720 cm^{-1}. It was identical with the formic acid cyclisation product of artobilochromen (mixed m.p., co-t.l.c., u.v., and n.m.r.). U.v., n.m.r., and mass spectral data are in the Tables. Acetylation of chromanoartobilochromen *b* (0.05 g) and recrystallisation of the product from diethyl ether–light petroleum (1 : 1) yielded *the triacetate* as a pale yellow solid (0.03 g), m.p. 125—127°, giving a negative reaction with $FeCl_3$ (Found: M^+, 562.183 7. $C_{31}H_{30}O_{10}$ requires M, 562.183 7); *m/e* 562(40%), 547(100), 520(13), 505(27), 478(12), 435(16), 421(7), 379(13), 219(14), and 203(47); for n.m.r. data see Table 3.

We thank Professors W. D. Ollis (University of Sheffield) and R. H. Thomson (University of Aberdeen), and Drs. P. Bladon (University of Strathclyde), and J. K. Mcleod (Australian National University) for n.m.r. and mass spectral data. Technical assistance from Mrs. S. C. Weerasekera, and Ms S. Ramachandran and Ms D. V. Ariyapala is acknowledged. The research programme has been supported by a grant from the National Science Council of Sri Lanka.

[6/1300 *Received*, 5*th July*, 1976]