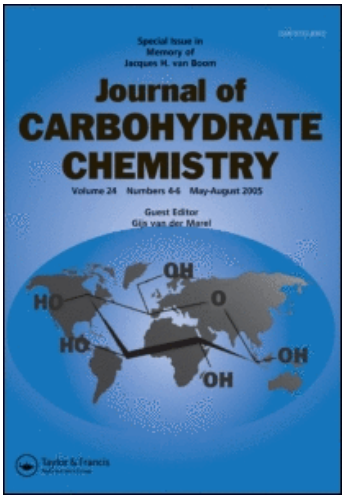

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2-GLYCOSYLCHROMENE DERIVATIVES

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ABSTRACT

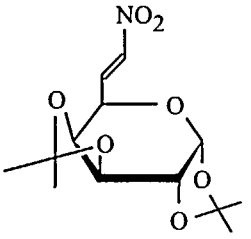
Treated with salicylaldehyde or its 5-methoxy derivative, a series of blocked terminal *(E)*-nitroenoses underwent a condensation reaction leading in fair to good yields to blocked 2-glycosyl-3-nitro-2H-chromene derivatives. Treated with cyanide, the nitro derivatives afforded 4-cyano-2-glycosyl-2H-chromenes *via* an addition-elimination reaction. These two types of chromenes bearing an electron-withdrawing group have been previously shown to have antiviral or cytotoxic properties related to their electrophilicity.

INTRODUCTION

We have shown that sugar derivatives bearing a soft electrophilic group can exhibit antiviral and/or cytotoxic properties[1] and that these activities can be quantitatively correlated with the spatial distribution of their electrophilicity.[2] Among these compounds were 2-glycosyl-3-nitro (or 4-cyano) chromene derivatives, synthesis of which will be described hereunder.

RESULTS AND DISCUSSION

The *(E)*-nitroenoses **1-6**[3,4] (Scheme 1) treated in alkaline medium with 5-methoxysalicylaldehyde underwent a tandem nucleophilic addition followed by an elimination reaction leading to the corresponding nitrochromenes **7-12**. Under the same



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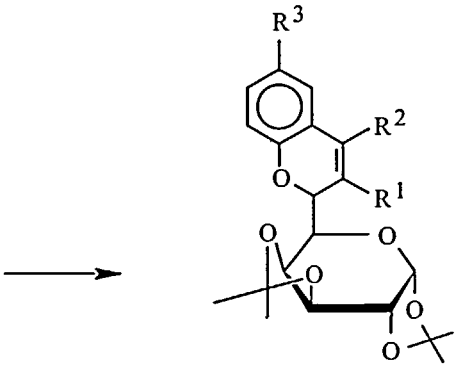

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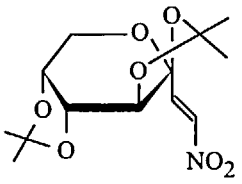
14 $R^1 = H$, $R^2 = CN$, $R^3 = OMe$



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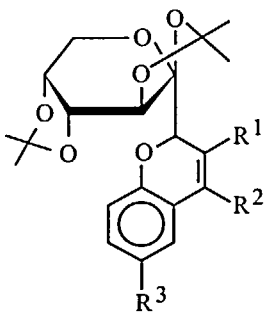

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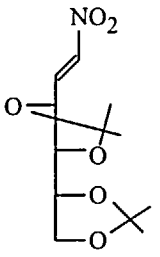

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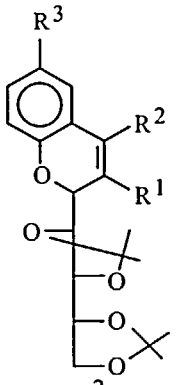
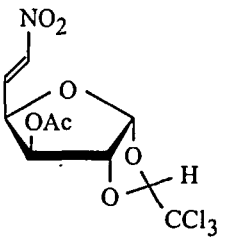


9 $R^1 = NO_2$, $R^2 = H$, $R^3 = OMe$

13 $R^1 = NO_2$, $R^2 = R^3 = H$

Scheme 1



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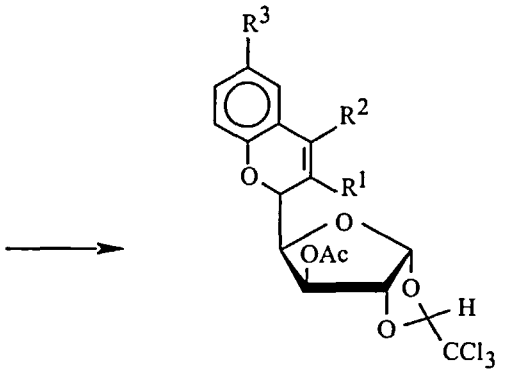

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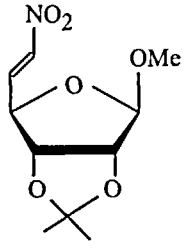
16 $R^1 = H$, $R^2 = CN$, $R^3 = OMe$



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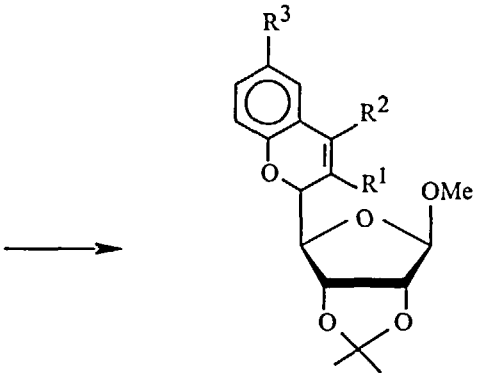
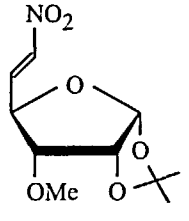


11 $R^1 = NO_2$, $R^2 = H$, $R^3 = OMe$



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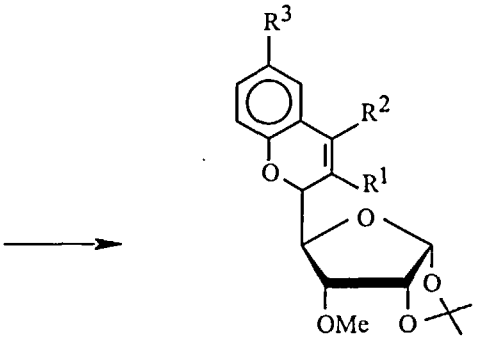
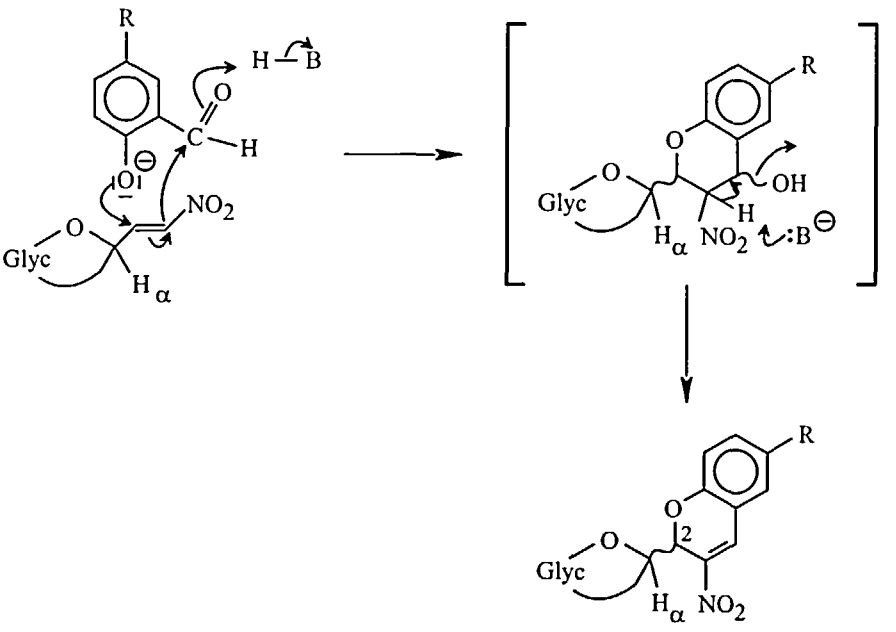


12 $R^1 = NO_2$, $R^2 = H$, $R^3 = OMe$

Scheme 1 (continued)



Scheme 2

conditions, **3** afforded **13** upon reaction with salicylaldehyde. Among the numerous procedures available for carrying out this Δ3-chromene synthesis and differing mostly in the nature of the basic catalyst, we chose those using basic alumina[5] complemented, in some instances, with triethylamine (Scheme 2). Some data pertaining to these reactions are collected in Table 1.

The reaction creates a novel asymmetric carbon on the chromene moiety and the stereochemistry of the reaction markedly depends on the steric hindrance of the groups located on the same face of the sugar ring as the nitroethenyl group of the starting material. The nitroenoses, numbered according to a decreasing hindrance on this face, give a totally stereoselective reaction with compounds **1** and **2**, no selectivity at all for compound **6**, and intermediate stereoselectivity for compounds **3-5**.

For both aldehydo sugars[6] and *E*-nitroenoses,[3,6] the preferred conformer is one in which the double bond almost eclipses the sugar C_α-O bond as shown by H NMR (including NOE) experiments. As we have established by quantum mechanical calculations that this peculiar conformational feature was provoked by orbital interactions,[7] we wanted to confirm that this rule held true in the crystalline state. X-ray diffraction studies (Table 2) of **2** (Fig. 1) and **4** (Fig. 2) showed that it was effectively the case. For compound **2** which

Table 1. Preparation of 3-nitrochromenes from nitroenoses [^{1}H NMR data (200 MHz)] relative to $CDCl_3$ solutions, J in Hz

Starting material	Product	Global yield	Isomer distribution[a]		Configuration[b]	$\delta_{H\alpha}$	$\delta_{H\text{-}2}$	$J_{\alpha,2}$
1	**7**	94%	M	1	*S*	3.99	5.82	6.8
			m	0				
2	**8**	65%	M	1	*S*		6.00	
			m	0				
3	**9**	60%	M	1	*S*	4.29	5.76	6.0
			m	0				
	13	91%	M	4	*S*	4.33	5.80	6.0
			m	1	*R*	4.33	5.82	1.5
4	**10**	81%	M	2	*R*	4.98	5.90	9.0
			m	1	*S*	4.92	5.90	5.3
5	**11**	31%	M	2	*R* ?	4.56[c]	4.96[c]	0[c]
			m	1	*S* ?	4.67[c]	5.00[c]	0[c]
6	**12**	73%		1	*R* ?	4.30	5.70	5.5
				1	*S* ?	4.26	5.87	3.2

a. M major, m, minor isomers. b. At C-2 of chromene moiety. c In C_6D_6.

possesses two C_α-O bonds, it is one C-O bond of the dioxolane ring which is almost eclipsed (dihedral angle 4.9°) by the nitrovinyl group. In the simpler case of **4**, the nitrovinyl group almost eclipses (dihedral angle 4.4°) the C_4-O bond. From this, the more accessible face of the double bond of the starting material can be easily determined. However, the orientation of the addition of carbon nucleophiles upon aldehydo sugars has been shown[3] not to be directed by the relative accessibilities of the diastereoisomeric faces of the carbonyl group in the most stable conformation but more probably by the stereoelectronic interactions developed along the reaction path by the incipient negative charge on the carbonyl oxygen atom.

Table 2. Summary of crystal data, intensity measurement and structure refinement for compounds **2**, **4**, **8** and **14**.

	2	**4**	**8**	**14**
Formula	$C_{13}H_{19}NO_7$	$C_{10}H_{10}NO_7Cl_3$	$C_{21}H_{25}NO_9$	$C_{22}H_{25}NO_7$
Mol. wt.	301.3	362.6	435.4	415.4
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space Group	$P\,2_12_12_1$	$P\,2_12_12_1$	$P\,2_1$	$P\,2_1$
a (Å)	9.9585(5)	8.3784(3)	9.438(2)	8.9268(7)
b (Å)	11.4521(7)	9.0476(5)	8.743(3)	11.1584(9)
c (Å)	12.9529(6)	19.0812(9)	13.033(2)	11.307(1)
β (°)	90	90	106.54(1)	113.147(4)
V (Å^3)	1477.2(1)	1446.4(1)	1030.9(4)	1035.6(1)
Z	4	4	2	2
F(000)	640	736	460	440
Dc gr.cm^{-3}	1.355	1.665	1.403	1.332
μ(CuKα) mm^{-1}	0.943	6.064	0.934	0.830
Tmin. , Tmax	0.7231 , 0.7754	0.2146 , 0.5044	0.7934 , 0.9414	0.7967 , 0.9240
$((\sin\theta)/\lambda)_{max}$ (Å^{-1})	0.531	0.531	0.531	0.531
Temperature (K)	200	200	200	200
No. measured reflc.	2201	2166	2791	2705
No. observed reflc.	1763	1651	2531	2382
Criterion for observed	$\|Fo\| > 4\sigma(Fo)$	$\|Fo\| > 4\sigma(Fo)$	$\|Fo\| > 4\sigma(Fo)$	$\|Fo\| > 4\sigma(Fo)$
Refinement (on F)	Full-matrix	Full-matrix	Full-matrix	Full-matrix
No. parameters	249	222	311	347
Weighting scheme	$\omega = 1/[\sigma^2(Fo)+0.0001(Fo^2)]$	$\omega = 1/[\sigma^2(Fo)+0.0001(Fo^2)]$	$\omega = 1/[\sigma^2(Fo)+0.0002(Fo^2)]$	$\omega = 1/[\sigma^2(Fo)+0.0001(Fo^2)]$
Max. and average Δ/σ	0.24 10^{-3} , 0.41 10^{-4}	0.26 10^{-2} , 0.16 10^{-3}	0.14 10^{-3} , 0.15 10^{-4}	0.36 10^{-2} , 0.31 10^{-3}
Max. and min. Δρ (e.Å^{-3})	0.11 , -0.10	0.21 , -0.19	0.20 , -0.18	0.12 , -0.14
S	2.60(7)	2.20(6)	2.20(5)	2.44(6)
Flack parameter (x) [15]	-0.07(29)	0.01(3)	0.06(36)	0.05(34)
R [a], ωR [b]	0.025 , 0.029	0.030 , 0.031	0.038 , 0.039	0.033 , 0.033

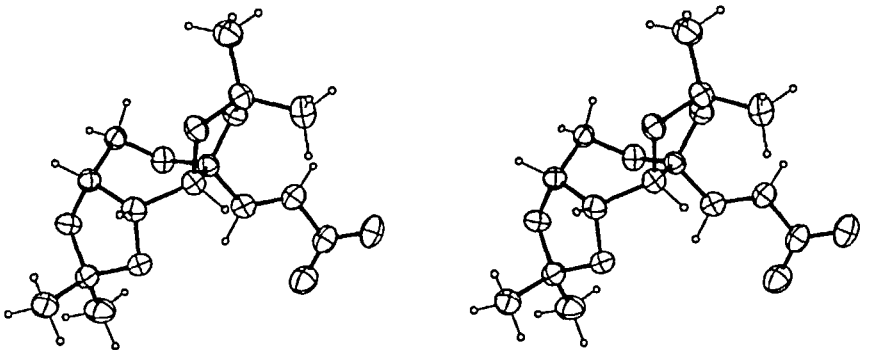


Figure 1. Stereoview of the structure of nitroenose derivative **2**

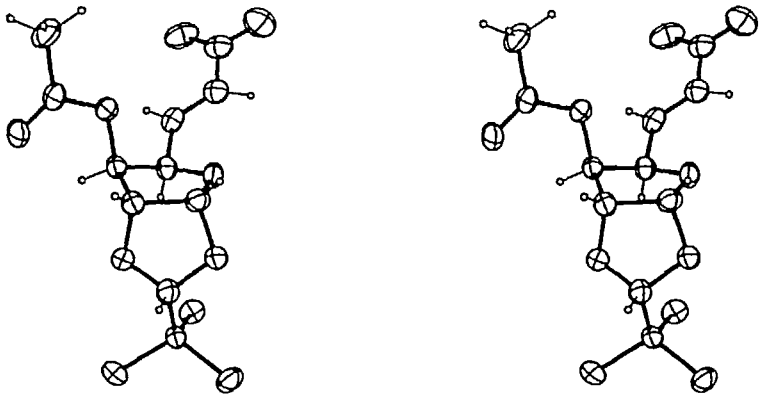


Figure 2. Stereoview of the structure of the nitroenose derivative **4**

The situation seems to be the same here. An attack on the more accessible (*re*) face of the electrophilic sp^2 carbon of **1** in its most stable conformation should lead to the (*2R*) isomer of **7**. In fact, an X-ray diffraction study (Table 2) of **14** (Fig. 3) prepared from **7** without configurational change, established its (*2S*) configuration. In the same way, an X-ray diffraction of **8** (Fig. 4) proved its (*2S*) configuration.

This indicates that the aryloxide nucleophile does not add to **1** in its most stable conformation, probably for stereoselective reasons and that successful addition leading to the product takes place on a substrate in which the nitrovinyl group has rotated away from the C_5-O bond presenting its *si* face to the aryloxide nucleophile. To undergo the cyclization step the intermediate carbanion should rotate presenting its nitro group on the

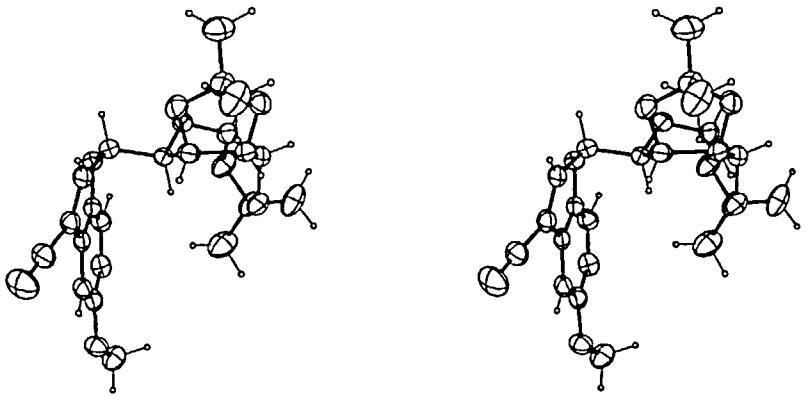


Figure 3. Stereoview of the structure of the cyanochromene derivative **14**

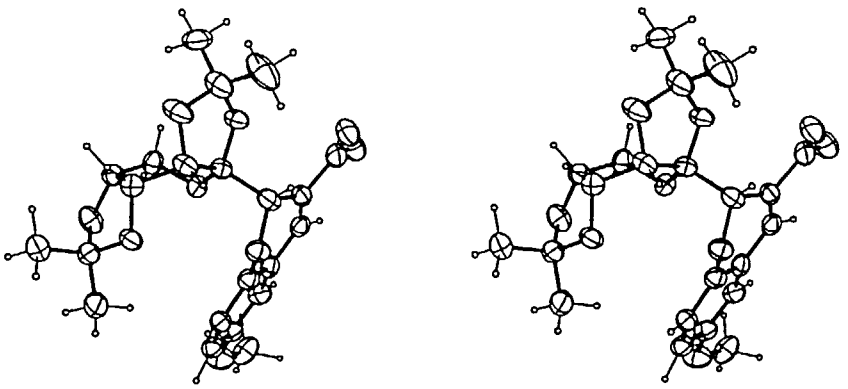


Figure 4. Stereoview of the structure of the nitrochromene derivative **8**

former *re* face. In other words, the reaction needs a large available space to accommodate the large nucleophile on the *si* face and some space on the back side for the nitro group when the cyclization takes place.

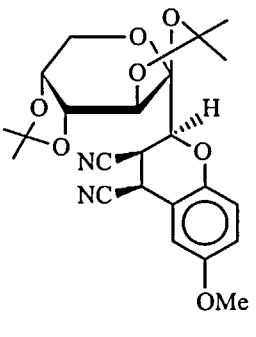
Data from Table 1 indicate that when two diasteroisomers are available, the only relatively discriminating features available are the $J_{\alpha,2}$ values which reflect the relative populations of antiperiplanar and synclinal conformers. In fact, only the major isomer of **10** and the minor isomer of **13** exist as pure conformers. Moreover, two half-chair forms of the pyran ring are possible and the relationships between the configuration at C-2 of the chromene moiety and the conformational equilibrium around the chromene-glycosyl bond

heavily depends on the conformation of the chromene moiety. The null values of the $J_{2,4}$ allylic coupling constants of 2-nitrochromenes and the intermediate value (3.0-4.8 Hz) of the vicinal $J_{2,3}$ coupling constants of the 3-cyanochromenes indicate that the pyran ring exists in the half-chair in which the glycosyl group adopts an axial position. The same conformation is found in the crystalline state for **8** and **14**. The conformation of the chromene moiety being known, examination of molecular models allowed configurational assignments, in some cases tentative, for compounds **9-13** (Table 1).

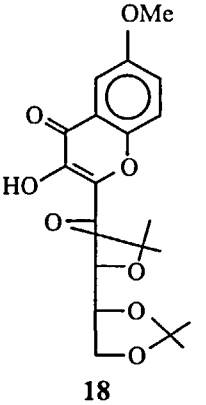
The electrophilicity of nitrochromenes, which can be appreciated using quantum mechanical techniques[2] and which is responsible for some biological activities of these compounds,[1,2] allowed their reaction with the cyanide nucleophile. Thus treated with potassium cyanide, **7**, **8**, and **10** afforded the 4-cyano-2-glycosylchromene derivatives **14** (55%), **15** (59%), and **16** (61%) respectively. The formation of these cyanochromenes implied the conjugate addition of a cyanide ion, immediately followed by the elimination of nitrous acid, as the product of the addition reaction could never be isolated.

Compound **17** resulting from a second nucleophilic attack of excess cyanide ion onto electrophilic **15**, was obtained in 21% yield as a by-product in the preparation of **15**. The small values of $J_{2,3}$ (3.0 Hz) and $J_{3,4}$ (5.0 Hz) are in favor of a configuration in which H-2, H-3, and H-4 are located on the same face of the dihydropyran ring (*2S, 3S, 4R* as the starting compound possesses a *(2S)* configuration).

Upon oxidation with hydrogen peroxide,[8] **9** afforded the flavonol analogue **18** (70%).



17



18

EXPERIMENTAL

General methods. Melting points (uncorrected) were determined under microscope with a *Mettler* P52 mp apparatus. TLC was performed on silica gel HF_{254} (*Merck*) with

detection by UV light and phosphomolybdic-sulfuric acid.[9] Dry column chromatography[10] was conducted on silica gel $60F_{254}$ (0.063-0.200 mm). IR spectra were recorded with a *Perkin-Elmer* FT-IR 1650. UV spectra were measured on a *Kontron* Uvicon 810 spectrophotometer. NMR were recorded at 20 °C on a *Bruker* WP 200 SY spectrometer (^{1}H 200 MHz), ^{13}C 50.4 MHz; chemical shifts in ppm from TMS; δ units, *b* broad, *s* singlet...). The MS were recorded on *Finnigan* 4023 of VG 70-70E spectrometers. Optical rotations were measured with a *Schmidt-Haensch* polarimeter. The circular dichroism (CD) measurements were obtained using a Jasco J-20 apparatus. ^{1}H NMR was performed on $CDCl_3$ solutions unless otherwise stated. IR frequencies are expressed in cm^{-1} and UV wavelengths in nm.

Crystal structure determinations of compounds 2, 4 , 8 and 14. Cell dimensions and intensities were measured at 200 K on an STOE Stadi4 diffractometer with graphite-monochromated Cu[Kα] radiation (λ = 1.5418 Å). Data were corrected for Lorentz and polarization effects and for absorption by analytical integration.[11] The structures were solved by direct methods using MULTAN 87,[12] all other calculations used XTAL[13] system and ORTEP[14] programs. A summary of crystal data, intensity measurement and structure refinement is given in Table 2. Perspective view of the crystal structures (Fig. 1, 2, 3, 4) are represented at 50% probability level. Crystallographic data (excluding structure factors) have been deposited to the *Cambridge Crystallographic Data Base* (deposition No. 109501, 109502, 109503 and109504 for compounds **2**, **4**, **8** and **14** respectively). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. + 44 (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

***(2S)*-2-(1,2:3,4-Di-*O*-isopropylidene-α-D-*galacto*-pentopyranos-5-*C*-yl)-6-methoxy-3-nitro-2H-chromene (7).** To a solution of **1** (1.1 g, 3.65 mmol) in CH_2Cl_2 (5 mL), 2-hydroxy-5-methoxybenzaldehyde (1.11 g, 7.3 mmol) and basic alumina (11 g) were added. After 5 h refluxing, followed by filtration and concentration, the residue submitted to dry column chromatography (1:10 AcOEt/hexane) afforded **7** (1.49 g, 94%): mp 179.0-179.5 °C; $[\alpha]_D^{21}$ -8.0° (*c* 1.1, $CHCl_3$); R_F 0.22 (1:4 AcOEt/hexane); UV (EtOH) 207 (20220), 243 (9250), 310 (8590), 402 (4420); CD (EtOH): $[\theta]_{235}$ 15220, $[\theta]_{287}$ -1410, $[\theta]_{340}$ -2720, and $[\theta]_{405}$ 2280; IR (KBr): 3055 ($\nu_{=C-H}$), 1637 ($\nu_{C=C}$), 1521 (ν_{asNO2}), 1388 and 1376 (δ_{CMe2}), and 1342 (ν_{sNO2}). ^{1}H NMR δ 0.94, 1.21, 1.31, and 1.45 (4 *s*, 4x3 H, 2 CMe_2), 3.79 (*s*, 3 H, OMe), 3.99 (*dd*, 1 H, $J_{5',2}$ 6.8 Hz, $J_{4',5'}$ 1.6 Hz, H-5'), 4.15 (*dd*, 1 H, $J_{3',4'}$ 8.0 Hz, H-4'), 4.24 (*dd*, 1 H, $J_{1',2'}$ 5.0 Hz, $J_{2',3'}$ 2.5 Hz, H-2'), 4.54 (*dd*, 1 H, H-3'), 5.46 (*d*, 1 H, H-1'), 5.82 (*d*, 1 H, H-2), 6.81 (*bd*, 1 H, $J_{5,7}$ 2.8 Hz, $J_{5,8}$ ca. 0.7 Hz, H-5), 6.97 (*dd*, 1 H, $J_{7,8}$ 9.2 Hz, H-7), 7.01 (*dd*, 1 H, H-8), and 7.87 (*s*, 1 H, H-4). MS: *m/z* (%) 59 (11), 71 (100), 85 (2), 160 (13), 171 (36), 206 (20), 229 (11), 316 (1), 420 (7, $M^{\cdot+}$ - $Me^{\cdot}$), and 435 (5, $M^{\cdot+}$).

Anal. Calcd for $C_{21}H_{25}NO_9$ (435.43): C, 57.93, H, 5.79; N, 3.22. Found: C, 57.64; H, 5.71; N, 3.15.

***(2S)*-2-(1,2:3,4-Di-*O*-isopropylidene-β-D-arabinopyranos-1-*C*-yl)-6-methoxy-3-nitro-2H-chromene (8).** To a solution of **2** (904 mg, 3 mmol) in CH_2Cl_2 (8 mL), 2-hydroxy-5-methoxybenzaldehyde (1.142 g, 7.5 mmol), basic alumina (7.75 g) and triethylamine (0.25 mL) were added. After 48 h refluxing, the reaction mixture was filtered, concentrated, and submitted to dry column chromatography (1:10 AcOEt/hexane) to afford, after recrystallization (ether/hexane) **8** (845 mg, 65%): mp 163.7-165.7 °C; $[\alpha]_D^{23}$ +76.3° (*c* 0.9, $CHCl_3$); R_F 0.26 (1:3 AcOEt/hexane); UV (EtOH). 211 (16660), 248 (8600), 313 (7600), and 406 (4250); CD (EtOH): $[\theta]_{213}$ -16700, $[\theta]_{239}$ -41000, $[\theta]_{267}$ -10000, $[\theta]_{301}$ -6700, $[\theta]_{347}$ 15000, $[\theta]_{460}$ 500; IR (KBr): 3060 ($\nu_{=C-H}$), 1646 ($\nu_{C=C}$), 1514 (ν_{asNO2}), 1382 and 1379 (δ_{CMe2}), and 1336 (ν_{sNO2}). ^{1}H NMR δ 1.25, 1.45, and 1.49 (3 *s*, 3 H, 6 H, 3 H, 2 CMe_2), 3.68 (*dd*, 1 H, $J_{5'a,5'b}$ 13.0 Hz, $J_{4',5'a}$ 1.0 Hz, Ha-5'), 3.79 (*s*, 3 H, OMe), 3.79 (*dd*, 1 H, $J_{4',5'b}$ 2.5 Hz, Hb-5'), 4.09 (*bdd*, 1 H, $J_{3',4'}$ 8.0 Hz, H-4'), 4.28 (*d*, 1 H, $J_{2',3'}$ 2.5 Hz, H-2'), 4.39 (*dd*, 1 H, H-3'), 6.00 (*s*, 1 H, H-2), 6.75 (*bd*, 1 H, H-5), 6.90 (*m*, 2 H, H-7, H-8), and 7.72 (*s*, 1 H, H-4). MS: *m/z* (%) 59 (99), 69 (14), 77 (3), 85 (87), 97 (5), 113 (40), 132 (3), 160 (19), 171 (100), 190 (3), 206 (17), 229 (31), 362 (3), and 420 (9, $M^{\cdot+}$ - $Me^{\cdot}$).

Anal. Calcd for $C_{21}H_{25}NO_9$ (435.43): C, 57.93; H, 5.79; N, 3.22. Found: C, 57.91; H, 5.84; N, 3.30.

***(2S)*-2-(1,2:3,4-Di-*O*-isopropylidene-D-*arabino*-1,2,3,4-tetrahydroxybut-1-*C*-yl)-6-methoxy-3-nitrochromene (9).** A solution of **3** (1.365 g, 5 mmol) in $CHCl_2$ (5 mL) treated with 2-hydroxy-5-methoxybenzaldehyde (1.52 g, 10 mmol) and basic alumina (15 g) as described for the preparation of **7** gave, after recrystallization (ether/hexane), **9** (1.23 g, 60%): mp 123.2-124.2 °C; $[\alpha]_D^{23}$ +20.8° (*c* 0.9, $CHCl_3$); R_F 0.26 (1:5 AcOEt/hexane); UV (EtOH): 207 (18100), 249 (8000), 317 (7600), 420 (3800); CD (EtOH): $[\theta]_{238}$ 21800, $[\theta]_{269}$ 6700, $[\theta]_{340}$ 7400, $[\theta]_{412}$ 1850; IR (KBr) 3068 ($\nu_{=C-H}$), 1652 ($\nu_{C=C}$), 1518 (ν_{asNO2}), 1378, 1370 (δ_{CMe2}), and 1342 (ν_{sNO2}). ^{1}H NMR δ 1.31, 1.40 (2 *s*, 2x6 H, 2 CMe_2), 3.79 (*s*, 3 H, OMe), 3.80 (*m*, 1 H, Ha-4'), 4.04 (*m*, 3 H, Hb-4', H-3', H-2'), 4.29 (*t*, 1 H, $J_{1',2'}$ 6.0 Hz, $J_{1',2'}$ 5.5 Hz, H-1'), 5.76 (*d*, 1 H, H-2), 6.75 (*d*, 1 H, $J_{5,7}$ 2.5 Hz, H-5), 6.85 (*d*, 1H, $J_{7,8}$ 9.0 Hz, H-7), 6.91 (*dd*, 1 H, H-8), and 7.80 (*s*, 1 H, H-4). ^{13}C NMR δ 25.23, 26.35, 26.71, 27.63 (2 CMe_2), 55.75 (OMe), 67.09 (C-4'), 72.81 (C-2), 76.77, 79.41 (C-1', C-2', C-3'), 109.76, 111.06 (2 CMe_2), 113.76 (C-8), 117.55 (C-7), 118.07 (C-4a), 120.23 (C-5), 129.28 (C-4), 140.33, 147.39 (C-6 and C-8a). MS: *m/z* (%) 57 (54), 73 (25), 85 (39), 101 (37), 115 (13), 132 (7), 143 (100), 160 (32), 190 (11), 206 (42), 334 (0.5), 392 (9, $M^{\cdot+}$ - $Me^{\cdot}$), and 407 (1, $M^{\cdot+}$).

Anal. Calcd for $C_{20}H_{25}NO_8$ (407.42): C, 58.96; H, 6.18; N, 3.44. Found: C, 58.93; H, 6.16; N,3.50.

(2R)*- and *(2S)*-2-[3-*O*-Acetyl-1,2-*O*-{*(1R)*-2,2,2-trichloroethylidene}-α-D-*xylo*-tetrofuranos-4-*C*-yl]-6-methoxy-3-nitro-2H-chromene (10).** To a solution of **4** (1.81 g, 5 mmol) in CH_2Cl_2 (15 mL), 2-hydroxy-5-methoxybenzaldehyde (1.31 g, 8.62 mmol) and basic alumina (13 g) were added. After 10 h under reflux, filtration and concentration, the residue was submitted to dry column chromatography (1:8 AcOEt/hexane) affording a fraction (320 mg) of pure ***(2R)*-10** which was recrystallized (ether/hexane) and a second fraction (1.69 g) consisting in a 3:2 mixture of ***(2R)*-10** and ***(2S)*-10**. Total yield: 81%; *(2R)/(2S)* ratio ca 2:1; R_F (1:3 AcOEt/hexane, 0.17 [(2S)*-10**] and 0.21 [***(2R)*-10**].

Pure ***(2R)*-10**: mp 194.2-195.5 °C; $[\alpha]_D^{22}$ -5.1° (*c* 1.0, $CHCl_3$); UV (EtOH): 205 (19300), 243 (8300), 311 (9000), and 405 (4300); CD (EtOH): $[\theta]_{233}$ 34800, $[\theta]_{265}$ -10600, $[\theta]_{295}$ -7600, $[\theta]_{332}$ -7600, $[\theta]_{355}$ -3900, and $[\theta]_{415}$ 2700; IR (KBr): 3073 ($\nu_{=C-H}$), 1750 ($\nu_{C=O}$), 1652 ($\nu_{C=C}$), 1527 (ν_{asNO2}), and 1337 (ν_{sNO2}). ^{1}H NMR δ 2.25 (*s*, 3 H, OAc), 3.82 (*s*, 3 H, OMe), 4.71 (*d*, 1 H, $J_{3',4'}$ 3.5 Hz, H-3'), 4.98 (*dd*, 1H, $J_{4',2}$ 9.0 Hz, H-4'), 5.25 (*s*, 1 H, $HCCl_3$), 5.51 (*d*, 1 H, $J_{1',2'}$ 3.8 Hz, H-2'), 5.90 (*d*, 1 H, H-2), 6.06 (*d*, 1 H, H-1'), 6.81 (*d*, 1 H, $J_{5,7}$ 3.0 Hz, H-5), 6.92 (*d*, 1 H, $J_{7,8}$ 9.0 Hz, H-8), 6.95 (*dd*, 1 H, H-7), and 7.87 (*s*, 1 H, H-4). MS: *m/z* (%) 55 (6), 73 (6), 83 (45), 101 (19), 143 (10), 160 (33), 190 (13), 206 (100), 289 (6), 467 (0.5), [495 (3) and 496 (3) $M^{\cdot+}$].

Anal. Calcd for $C_{18}H_{16}Cl_3NO_9$ (496.69): C, 43.53; H, 3.25; Cl, 21.41; N, 2.82. Found: C, 43.80; H, 3.33; Cl, 21.48; N, 2.85.

^{1}H NMR of ***(2S)*-10** (in a 3:2 *(2R)/(3R)* mixture) δ 2.22 (*s*, 3 H, OAc), 3.80 (*s*, 3 H, OMe), 4.70 (*d*, 1 H, $J_{3',4'}$ 3.8 Hz, H-3'), 4.92 (*dd*, 1 H, $J_{4',2}$ 5.3 Hz, H-4'), 5.28 (*s*, 1 H, $HCCl_3$), 5.39 (*d*, 1 H, $J_{1',2'}$ 3.8 Hz, H-2'), 5.90 (*d*, 1 H, H-2), 5.98 (*d*, 1 H, H-1'), 6.79 (*d*, 1 H, $J_{5,7}$ 2.5 Hz, H-5), 6.93 (*m*, 2 H, H-7, H-8), and 7.90 (*s*, 1 H, H-4).

***(2R)*- and *(2S)*-6-Methoxy-2-(methyl 2,3-*O*-isopropylidene-β-D-*ribo*-tetrofuranosid-4-*C*-yl)-3-nitro-2H-chromene (11).** To a solution of **5** (1.18 g, 4.81 mmol) in CH_2Cl_2 (13 mL), 2-hydroxy-5-methoxybenzaldehyde (1.27 g, 8.36 mmol) and basic alumina (13 g) were added. After 4 h under reflux, dry column chromatography (1:20 AcOEt/hexane) afforded **11** (560 mg, 31%) as a 2:1 ***(2R?)/(2S?)*-11** mixture: syrup, R_F 0.61 (1:2 AcOEt/hexane); UV (EtOH): 207 (21000), 246 (8900), 317 (8500), and 418 (3900); IR (film): 3070 ($\nu_{=C-H}$), 1646 ($\nu_{C=C}$), 1519 (ν_{asNO2}), 1383, 1374 (δ_{CMe2}), and 1335 (ν_{sNO2}). ^{1}H NMR (C_6D_6) δ ***(2R?)*-11**: 1.30, 1.39 (2 *s*, 2x3 H, CMe_2), 3,36 (*s*, 3 H, MeO-1'), 3.80 (*s*, 3 H, MeO-6), 4.39 (*dd*, 1 H, $J_{1',2'}$ 8.0 Hz, $J_{2',3'}$ 2.0 Hz, H-2'), 4.56 (*d*, 1 H, $J_{3',4'}$ 6.0 Hz, H-4'), 4.96 (*s*, 1 H, $J_{4',2}$ ca. 0 Hz, H-2), 4.97 (*dd*, 1 H, H-3'), 5.55 (*d*, 1 H, H-1'), 6.80 (*m*, 1 H, H-5), 6.95 (*m*, 2 H, H-7, H-8), 7.82 (*s*, 1 H, H-4). ***(2S?)*-11**: 1.30, 1.40 (2 *s*, 2x3 H, CMe_2), 3.34 (*s*, 3 H, MeO-1'), 3.80 (*s*, 3 H, MeO-6), 4.39 (*dd*, 1 H, $J_{1',2'}$ 8.0 Hz, $J_{2',3'}$ 2.0 Hz, H-2'), 4.67 (*d*, 1 H, $J_{3',4'}$ 6.0 Hz, H-4'), 4.76 (*dd*, 1 H, H-3'), 5.00 (*s*, 1 H, $J_{4',2}$ ca. 0 Hz, H-2), 5.66 (*d*, 1 H, H-1'), 6.80 (*m*, 1 H, H-5), 6.95 (*m*, 2 H, H-7, H-8), and 7.96 (*s*,

1 H, H-4). MS: *m/z* (%) 59 (98), 69 (26), 87 (59), 95 (14), 103 (7), 115 (71), 133 (19), 141 (9), 149 (25), 173 (100), 191(13), 206 (30), 279 (4), 364 (3, $M^{\cdot+}$ - Me·), and 379 (1, $M^{\cdot+}$).

Anal. Calcd for $C_{18}H_{21}NO_8$ (379.37): C, 56.99; H, 5.58; N, 3.69. Found: C, 57.28; H, 5.74; N, 3.46.

***(2R)*- and *(2S)*-2-(1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-*ribo*-tetrofuranos-4-*C*-yl)-6-methoxy-3-nitro-2H-chromene (12).** To a solution of **6** (450 mg, 1.84 mmol) in CH_2Cl_2 (5 mL), 2-hydroxy-5-methoxybenzaldehyde (304 mg, 2 mmol), basic alumina (5 g), and triethylamine (0.5 mL) were added. After 10 h stirring at 22 °C, the reaction mixture was filtered, concentrated, and submitted to dry column chromatography (1:4 AcOEt/hexane) to give **12** (534 mg, 73%) as a 1:1 diastereoisomeric mixture which was further purified by short-path distillation (240 °C, 10^{-2} mmHg): mp 64.1-67.2 °C; R_F 0.33 (1:1 AcOEt/hexane; UV (EtOH): 207 (21000), 247 (8600), 318 (9400), and 425 (4400); IR (KBr): 3067 ($\nu_{=C-H}$), 1656 ($\nu_{C=C}$), 1512 (ν_{asNO2}), 1385, 1374 (δ_{CMe2}), and 1330 (ν_{sNO2}). ^{1}H NMR (1:1 mixture of *A* and *B* isomers) δ 1.30, 1.31, 1.43, 1.52 (4 s, 4x3 H, 2 CMe_2) (*A* and *B*), 3.21, 3.43 (2 *s*, 2x3 H, MeO-3') (*A* and *B*), 3.79, 3.80 (2 *s*, 2x3 H, MeO-6) (*A* and *B*), 3.60 (*dd*, 1 H, $J_{2',3'}$ 4.2 Hz, $J_{3',4'}$ 9.0 Hz, H-3') (*B*), 3.85 (*dd*, 1 H, $J_{2',3'}$ 4.0 Hz, $J_{3',4'}$ 9.0 Hz, H-3') (*A*), 4.26 (*dd*, 1 H, $J_{4',2}$ 3.2 Hz, H-4') (*B*), 4.30 (*dd*, 1 H, $J_{4',2}$ 5.5 Hz, H-4') (*A*), 4.62 (*t*, 1 H, $J_{1',2'}$ 3.8 Hz, H-2') (*B*), 4.70 (*t*, 1 H, $J_{1',2'}$ 3.8 Hz, H-2') (*A*), 5.60 (*d*, 1 H, H-1') (*A*), 5.70 (*d*, 1 H, H-2) (*A*), 5.75 (*d*, 1 H, H-1') (*B*), 5.87 (*d*, 1 H, H-2) (*B*), 6.75, 6.79 (2 *t*, 2x1 H, $J_{5,7} = J_{5,8}$ 1.7 Hz, H-5) (*A* and *B*), 6.90-6.94 (*m*, 4 H, H-7, H-8) (*A* and *B*), 7.86, 7.88 (2 *s*, 2x1 H, H-4) (*A* and *B*). MS: *m/z* (%) 59 (35), 73 (5), 87 (100), 103 (8), 115 (49), 160 (11), 173 (57), 206 (12), 243 (8), 275 (5), 364 (15, $M^{\cdot+}$ - Me·), and 379 (26, $M^{\cdot+}$).

Anal. Calcd for $C_{18}H_{21}NO_8$ (379.37): C, 56.99; H, 5.58; N, 3.69. Found: C, 57.26; H, 5.72; N, 3.74.

***(2S)*- and *(2R)*-2-(1,2:3,4-Di-*O*-isopropylidene-D-*arabino*-1,2,3,4-tetrahydroxy-but-1-*C*-yl)-3-nitro-2H-chromene (13).** To a solution of **3** (820 mg, 3 mmol) in CH_2Cl_2 (8 mL), salicylaldehyde (2.23 g, 18.26 mmol), basic alumina (7.75 g) and triethylamine (0.2 mL) were added. After 5 h reflux, filtration, and concentration, the residue was submitted to dry column chromatography (1:5 AcOEt/hexane) to give **13** (1.03 g, 91%) as a 4:1 syrupy mixture of *(2S)*- and *(2R)*-**13**: Eb 160 °C/10^{-2} mmHg; R_F (1:2 AcOEt/hexane) 0.77 (*(2R)*-**13**) and 0.67 (*(2S)*-**13**); UV (EtOH): 207 (15300), 249 (7950), 314 (6650), and 389 (4900); IR (film): 3077 ($\nu_{=C-H}$), 1653 ($\nu_{C=C}$), 1520 (ν_{asNO2}), 1382, 1372 (δ_{CMe2}), and 1327 (ν_{sNO2}). ^{1}H NMR δ *(2S)*-**13** 1.30, 1.33, 1.39, 1.41 (4 *s*, 4x3 H, 2 CMe_2), 3.82 (*dt*, 1 H, $J_{3',4'a} \sim J_{3',4'b}$ 4.8 Hz, $J_{2',3'}$ 2.5 Hz, H-3'), 4.05 (*m*, 3 H, Ha-4', Hb-4', H-2'), 4.33 (*t*, 1 H, $J_{1',2'}$ 6.0 Hz; $J_{1'2}$, 6.0 Hz, H-1'), 5.82 (*d*, 1 H, H-2), 6.97, 7.32 (2 *m*, 2x2 H, Ar), and 7.86 (*s*, 1

H, H-4); *(2R)*-**13** 1.30, 1.33, 1.39, 1.41 (4 *s*, 4x3 H, 2 CMe_2), 3.82 (*dt*, 1 H, $J_{3',4'a} \sim J_{3',4'b}$ 4.8 Hz, $J_{2',3'}$ 2.5 Hz, H-3'), 4.05 (*m*, 3 H, Ha-4', Hb-4', H-2'), 4.33 (*dd*, 1 H, $J_{1',2'}$ 6.0 Hz, $J_{1',2}$ 1.5 Hz, H-1'), 5.80 (*d*, 1 H, H-2), 6.97, 7.32 (2 *m*, 2x2 H, Ar), 7.93 (*s*, 1 H, H-4). MS: *m/z* (%) 57 (54), 72 (9), 85 (12), 101 (13), 115 (9), 130 (6), 143 (100), 176 (7), 201 (7), 362 (12, $M^{\cdot+}$ - Me·), and 377 (0.5, $M^{\cdot+}$).

Anal Calcd for $C_{19}H_{23}NO_7$ (377.40): C, 60.47; H, 6.14; N, 3.71. Found: C, 60.59; H, 6.18; N, 3.77.

***(2S)*-4-Cyano-2-(1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-pentopyranos-5-*C*-yl)-6-methoxy-2H-chromene (14).** To a solution of potassium cyanide (640 mg, 9.8 mmol) and tetrabutylammonium bromide (60 mg, 0.19 mmol) in water (12 mL) at pH 9-9.5 (adjusted by addition of 10% aqueous HCl) was added a solution of **7** (380 mg, 0.87 mmol) in a mixture of toluene (25 mL) and THF (12 mL). After 10 h, the reaction mixture was concentrated and submitted to dry column chromatography (1:10 AcOEt/hexane). Recrystallization (ether/hexane) of the major fraction obtained gave **14** (200 mg, 55%): mp 161.4-162.8 °C; $[\alpha]_D^{24}$ -301.7° (*c* 0.9, $CHCl_3$); R_F 0.58 (1:2 AcOEt/hexane); UV (EtOH): 204 (21300), 224 (15700), 248 (14000), 280 (2850), and 350 (2050); DC (EtOH): $[\theta]_{217}$ -19700, $[\theta]_{250}$ -18200, $[\theta]_{270}$ -14600, $[\theta]_{283}$ -12100, and $[\theta]_{345}$ -13650; IR (KBr) 3062 ($\nu_{=C-H}$), 2234 ($\nu_{C\equiv N}$), 1623 ($\nu_{C=C}$), 1382, 1374 (δ_{CMe2}). ^1H NMR δ 1.27, 1.36, 1.49 (3 *s*, 6 H, 3 H, 3 H, 2 CMe_2), 3.80 (*s*, 3 H, OMe), 4.05 (*dd*, 1 H, $J_{4',5'}$ 2.0 Hz, $J_{5',2}$ 8.2 Hz, H-5'), 4.24 (*dd*, 1 H, $J_{3',4'}$ 7.7 Hz, H-4'), 4.32 (*dd*, 1 H, $J_{1',2'}$ 5.0 Hz, $J_{2',3'}$ 2.5 Hz, H-2'), 4.61 (*dd*, 1 H, H-3'), 5.05 (*dd*, 1 H, $J_{2,3}$ 4.8 Hz, H-2), 5.58 (*d*, 1 H, H-1'), 6.73 (*d*, 1 H, H-3), 6.82 (*dd*, 1 H, $J_{7,8}$ 8.5 Hz, $J_{5,7}$ 3.0 Hz, H-7), 6.88 (*bd*, 1 H, $J_{5,8}$ 0.7 Hz, H-5), and 6.95 (*dd*, 1 H, H-8). MS: *m/z* (%) 59 (9), 71 (100), 143 (7), 171 (30), 186 (30), 229 (11), 254 (18), 282 (27), 300 (9), 342 (18), 400 (54, $M^{\cdot+}$ - Me·), and 415 (45, $M^{\cdot+}$).

Anal. Calcd for $C_{22}H_{25}NO_7$ (415.45): C, 63.61; H, 6.07; N, 3.37. Found: C, 63.58; H, 5.98; N, 3.40.

***(2S)*-4-Cyano-2-(1,2:3,4-di-*O*-isopropylidene-β-D-arabinopyranos-1-*C*-yl)-6-methoxy-2H-chromene (15).** To a solution of potassium cyanide (4 g, 61.4 mmol) and tetrabutylammonium bromide (96 mg, 0.3 mmol) in water (20 mL) at pH 9-9.5 (adjusted by addition of 10% aqueous HCl) was added a solution of **8** (680 mg, 1.37 mmol) in a mixture of toluene (40 mL) and THF (20 mL) was added. After 24 h at 24 °C, the reaction mixture was concentrated and submitted to dry column chromatography (1:8 AcOEt/hexane) to give **15** (350 mg, 59%) and **17** (130 mg, 21%). A short-path distillation (230 °C, 5.10^{-4} mmHg) afforded the analytical sample of **15**: mp 61.4-62.6 °C; $[\alpha]_D^{27}$ +82° (*c* 1.1, $CHCl_3$); R_F 0.57 (1:2 AcOEt/hexane); UV (EtOH): 205 (19350), 223 (16000), 246 (15350), 280 (2750), and 348 (1800); CD (EtOH): $[\theta]_{215}$ -5750, $[\theta]_{244}$ 8300, $[\theta]_{277}$ 3700, and $[\theta]_{350}$ 4350; IR (KBr): 3083 ($\nu_{=C-H}$), 2228 ($\nu_{C\equiv N}$), 1612 ($\nu_{C=C}$), 1383, 1374 (δ_{CMe2}).

^{1}H NMR δ 1.29, 1.30, 1.38, 1.46 (4 *s*, 4x3 H, 2 CMe_2), 3.80 (*s*, 3 H, OMe), 3.82 (*dd*, 1 H, $J_{4',5'a}$ 1.0 Hz, $J_{5'a,5'b}$ 7.8 Hz, Ha-5'), 3.94 (*dd*, 1 H, $J_{4'5'b}$ 2.0 Hz, Hb-5'), 4.28 (*bd*,1 H, $J_{3',4'}$ 7.0 Hz, H-4'), 4.69 (*m*, 2 H, H-2', H-3'), 5.08 (*d*, 1 H, $J_{2,3}$ 3.0 Hz, H-2), 6.78 (*d*, 1 H, H-3), and 6.67-6.90 (*m*, 3 H, Ar). MS: *m/z* (%) 59 (23), 85 (36), 113 (21), 143 (7), 171 (100), 186 (21), 282 (5), 400 (9, $M^{\cdot+}$ - Me·), and 415 (1, $M^{\cdot+}$).

Anal. Calcd for $C_{22}H_{25}NO_7$ (415.45): C, 63.61; H, 6.07; N, 3.37. Found: C, 63.63; H, 6.08; N, 3.38.

***(2R)*- and *(2S)*-2-[3-*O*-Acetyl-1,2-*O*-{*(1R)*-2,2,2-trichloroethylidene}-α-D-*xylo*-tetrofuranos-4-*C*-yl]-4-cyano-6-methoxy-2H-chromene (16).** Prepared as described for **14** from **10** (3:2*(2R)/(2S)* mixture, 680 mg, 1.37 mmol), potassium cyanide (1.95 g, 29.9 mmol) and tetrabutylammonium bromide (91 mg, 0.28 mmol). After 48 h reaction, a dry column chromatography (1:5 ether/hexane) afforded **16** (400 mg, 61%) as a 5:4 *(2R)/(2S)*-**16** mixture: mp 180.5-183.6 °C; R_F 0.33 (1:2 AcOEt/hexane; UV (EtOH) 205 (16800), 223 (12500), 248 (11900), 280 (2700), 350 (1550); IR (KBr) 3079 ($\nu_{=C-H}$), 2231 ($\nu_{C\equiv N}$), 1752 ($\nu_{C=O}$), and 1612 ($\nu_{C=C}$). ^{1}H NMR δ *(2R)*-**16** 2.14 (*s*, 3 H, OAc), 3.81 (*s*, 3 H, OMe), 4.75 (*d*, 1 H, $J_{1',2'}$ 4.0 Hz, H-2'), 4.91 (*dd*, 1 H $J_{3',4'}$ 3.3 Hz, $J_{4',2}$ 9.0 Hz, H-4'), 5.02 (*dd*, 1 H, $J_{2,3}$ 3.5 Hz, H-2), 5.36 (*s*, 1 H, $HCCCl_3$), 5.68 (*d*, 1 H, H-3'), 6.16 (*d*, 1 H, H-1'), 6.69 (*d*, 1 H, H-3), and 6.75-6.90 (*m*, 3 H, H-5', H-7, H-8); *(2S)*-**16** 2.11 (*s*, 3 H, OAc), 3.81 (*s*, 3 H, OMe), 4.75 (*d*, 1 H, $J_{1',2'}$ 4.0 Hz, H-2'), 4.98 (*dd*, 1 H, $J_{3',4'}$ 3.5 Hz, $J_{4',2}$ 7.0 Hz, H-4'), 5.12 (*dd*, 1 H, $J_{2,3}$ 3.8 Hz, H-2), 5.36 (*s*, 1 H, $HCCCl_3$), 5.52 (*d*, 1 H, H-3'), 6.18 (*d*, 1 H, H-1'), 6.49 (*d*, 1 H, H-3), and 6.75-6.90 (*m*, 3 H, H-5, H-7, H-8). MS: *m/z* (%) 83 (25), 101 (16), 143 (22), 186 (100), 228 (7), 270 (25), 289 (62), 358 (16), and 475 (16, $M^{\cdot+}$).

Anal. Calcd for $C_{19}H_{16}Cl_3NO_7$ (476.70): C, 47.87; H, 3.38; Cl, 22.31; N, 2.94. Found: C, 47.67; H, 3.35; Cl 22.10; N, 2.87.

3,4-Dicyano-2-(1,2:3,4-di-*O*-isopropylidene-β-D-arabinopyranos-1-*C*-yl)-6-methoxychromane (17). Obtained as described for the preparation of **15**: mp 163.0-164.8 °C; $[\alpha]_D^{30}$ +20.4° (*c* 0.9, $CHCl_3$); R_F 0.31 (1:2 AcOEt/hexane); UV (EtOH): 204 (17000), 230 (9000), and 294 (3600); IR (KBr): 2234 ($\nu_{C\equiv N}$), 1384, 1374 (δ_{CMe2}). ^{1}H NMR δ 0.93, 1.13, 1.19, 1.39 (4 *s*, 4x3 H, 2 CMe_2), 3.21 (*s*, 3 H, OMe), 3.68 (*bs*, 2 H, H2-5'), 3.75 (*m*, 1 H, $J_{3',4'}$ 8.0 Hz, H-4'), 3.80 (*dd*, 1 H, $J_{2,3}$ 3.0 Hz, $J_{3,4}$ 5.0 Hz, H-3), 4.40 (*dd*, 1 H, $J_{2',3'}$ 3.0 Hz, H-3'), 4.42 (*d*, 1 H, H-4), 4.63 (*d*, 1 H, H-2'), 4.83 (*d*, 1 H, H-2), 6.65 (*m*, 2 H, H-6, H-7), 6.94 (*bs*, 1 H, H-5). MS: *m/z* (%) 59 (45), 69 (11), 85 (34), 97 (14), 113 (21), 143 (27), 171 (100), 186 (48), 213 (41), 229 (20), 241 (18), 282 (9), 309 (11), 427 (37, $M^{\cdot+}$ - Me·), 442 (54, $M^{\cdot+}$).

Anal. Calcd for $C_{23}H_{26}N_2O_7$ (442.47): C, 62.43; H, 5.92; N, 6.33. Found: C, 62.46; H, 5.90; N, 6.41.

3-Hydroxy-2-(1,2:3,4-di-*O*-isopropylidene-D-*arabino*-1,2,3,4-tetrahydroxybut-1-yl)-6-methoxy-4H-benzo[b]pyran-4-one (18). To a solution of **9** (580 mg, 1.42 mmol) in methanol (10 mL) a 15% aqueous solution of hydrogen peroxide (2 mL) and a 2M aqueous solution of sodium hydroxide (1 mL) were added. After 30 min stirring, the reaction medium was neutralized (Dowex 50 [H^+], filtered, concentrated, and submitted to dry column chromatography (1:5 AcOEt/hexane) to give **18** (390 mg, 70%): mp 145.5-147.0 °C; $[\alpha]_D^{25}$ +11.5° (*c* 0.4, $CHCl_3$); R_F 0.1 (1:5 AcOEt/hexane); UV (EtOH): 248 (21150), 295 (7400), and 340 (7100); IR (KBr): 3296 (ν_{O-H}), 1631 ($\nu_{C=O}$), 1381, and 1372 (δCMe2). ^1H NMR δ 1.12, 1.29, 1.55, 1.60 (4 *s*, 4x3 H, 2 CMe_2), 2.93 (*s*, 3 H, OMe), 4.02 (*dd*, 1 H, $J_{4'a,4'b}$ 8.2 Hz, $J_{3',4'a}$ 4.0 Hz, Ha-4'), 4.13 (*dd*, 1 H, $J_{3',4'b}$ 6.0 Hz, Hb-4'), 4.28 (*ddd*, 1 H, $J_{2',3'}$ 7.2 Hz, H-3'), 4.50 (*dd*, 1 H, $J_{1',2'}$ 8.0 Hz, H-2'), 5.35 (*d*, 1 H, H-1'), 6.43 (exchangeable *bs*, 1 H, OH), 7.31 (*dd*, 1 H, $J_{5,7}$ 3.2 Hz, $J_{7,8}$ 9.0 Hz, H-7), 7.46 (*d*, 1 H, H-8), and 7.55 (*d*, 1 H, H-5. MS: *m/z* (%) 59 (94), 73 (50), 79 (25), 101 (100), 121 (18), 135 (28), 151 (61), 161 (14), 177 (33), 192 (40), 205 (59), 217 (68), 233 (83), 245 (20), 262 (31), 277 (21), 318 (19), 333 (9), 376 (12), 392 (0.5, $M^{\cdot+}$).

Anal. Calcd for $C_{20}H_{24}O_8$ (392.41): C, 61.22; H, 6.16. Found: C, 61.09; H, 6.13.

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