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INTERACTION OF INDOLES WITH GLYCOSYL HALIDES IN THE PRESENCE OF SILVER OXIDE

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ABSTRACT

The reaction of indole with 2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl bromide in the presence of silver oxide yielded a mixture of *O*-acetylated 1-α-L-arabinopyranosylindole, 3-α-L-arabinopyranosylindole (the first indole *C*-nucleoside), and 1,2-*O*-[1-(indol-1-yl)ethylidene]-β-L-arabinopyranose. The corresponding derivatives were obtained from 5- or 6-nitroindole Likewise, 6-nitroindole and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide gave *O*-acetylated 1,2-*O*-[1-(6-nitroindol-1-yl)-ethylidene]-α-D-glucose and 1,2-*O*-[1-(6-nitroindol-3-yl)ethylidene]-α-D-glucose, and 6-nitroindole with 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl bromide gave *O*-benzoylated 1,2-*O*-[6-nitroindol-1-yl(phenyl)methylidene]-α-D-ribofuranose and its 6-nitroindol-3-yl analogue Only 1,2-*O*-[indol-1-yl(phenyl)methylidene]-α-D-ribofuranose was isolated after the condensation of indole with 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl bromide The deacetylation of the above compounds afforded the corresponding *N*- and *C*-nucleosides or 1,2-*O*-alkylidene derivatives

INTRODUCTION

Indole nucleosides have been widely studied and are usually prepared by the indoline–indole method[1,2]. Attempts to synthesise an indole nucleoside from an acylglycosyl halide and an indole salt were unsuccessful, although the reaction[3] of indolylmagnesium halide and tetra-*O*-acetyl-α-D-glucopyranosyl bromide gave 1-D-glucopyranosylindole Recently, *O*-benzoylated 4-nitro-1-β-D-ribofuranosylindole was obtained by treatment of 4-nitroindole with 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl bromide in the presence of silver oxide and molecular sieve[4], and we now report another application of this method Nitroindole nucleosides are of interest because the 1-α-L-arabinopyranosides of 5- or 6-nitroindole inhibit the growth of some solid tumours in mice[5,6].

RESULTS AND DISCUSSION

Indole reacted with 2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl bromide in the presence of silver oxide and molecular sieve in dry benzene to yield 1-(2,3,4-tri-*O*-

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TABLE I

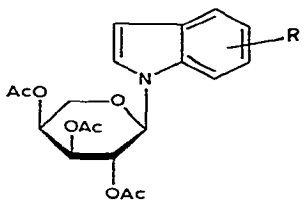
DATA FOR NEW INDOLE DERIVATIVES

Compound	M p (degrees)	$[\alpha]_D^{20}$ (c 1) (degrees)	Found (%) C	H	N	Calc (%) C	H	N	Formula
5	175–176	−65 (CHCl3)	54 4	4 9	7 1	54 3	4 8	6 7	$C_{19}H_{20}N_2O_9$
6	[a]	+25 5 (CHCl3)	54 0	4 8	6 9	54 3	4 8	6 7	$C_{19}H_{20}N_2O_9$
7	[a]	+22 (CHCl3)	60 9	5 8		60 8	5 8		$C_{19}H_{21}N_1O_7$
8	[a]	−23 (CHCl3)	54 4	4 9		54 3	4 8		$C_{19}H_{20}N_2O_9$
9	[a]	−10 (CHCl3)	51 9	4 8	6 5	52 1	5 1	6 4	$C_{19}H_{20}N_2O_9$ H_2O
11	[a]	+29 (EtOH)	53 6	4 9	8 4	53 6	4 8	8 3	$C_{15}H_{16}N_2O_7$
12	170–171	+43 (Me_2CO)	53 3	4 9	8 6	53 6	4 8	8 3	$C_{15}H_{16}N_2O_7$
13	[a]	+41 5 (MeOH)							
14	[a]	+44 (MeOH)							
15	230–231	−48 (c 0 5, C_5H_5N)	52 5	4 8		52 4	4 9		$C_{13}H_{14}N_2O_6$ $0\,2H_2O$
16	185–186	+26 ($CHCl_3$)	53 8	4 9	5 9	53 7	4 9	5 7	$C_{22}H_{24}N_2O_{11}$
18	[a]	+39 (MeOH)	49 5	5 1		49 4	5 3		$C_{16}H_{18}N_2O_8$ $1\,25H_2O$
19	[a]	+89 ($CHCl_3$)	67 3	4 6	4 7	67 3	4 3	4 6	$C_{34}H_{26}N_2O_9$
21	[a]	+79 ($CHCl_3$)	72 0	4 9	2 7	72 1	4 9	2 5	$C_{34}H_{27}N_1O_7$ $0\,25H_2O$
23	[a]	+43 (MeOH)	60 2	4 8	7 0	60 3	4 6	7 0	$C_{20}H_{18}N_2O_7$
24	[a]	+16 (c 1 83, MeOH)	64 7	5 6	3 8	64 7	5 7	3 8	$C_{20}H_{19}N_1O_5$ H_2O
26	[a]	−12 (MeOH)	63 4	4 7	5 8	63 4	4 5	5 5	$C_{27}H_{22}N_2O_8$ $0\,5H_2O$
27	[a]	+23 (MeOH)	57 7	4 9	6 7	57 6	4 8	6 7	$C_{20}H_{18}N_2O_8$ H_2O

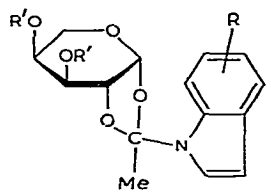
[a] Amorphous

acetyl-α-L-arabinopyranosyl)indole (**1**), 3-(2,3,4-tri-*O*-acetyl-α-L-arabinopyranosyl)-indole (**7**), and 3,4-di-*O*-acetyl-1,2-*O*-[1-(indol-1-yl)ethylidene]-β-L-arabinopyranose (**4**) The products were separated by p l c Similarly, 5- or 6-nitroindole yielded a mixture of *O*-acetylated 1-nucleoside **2** or **3**, *C*-nucleoside **8** or **9**, and (nitroindol-1-yl)ethylidene derivative **5** or **6** Some properties of these compounds are presented in Table I The major product from indole was **1** (15%), and only 2% of **4** (contaminated with indole) was obtained The major reaction products from nitroindoles

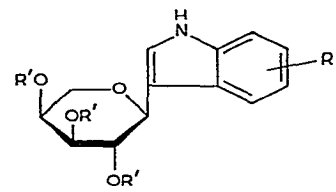
were **5** or **6** (40%) The yields of the *C*-nucleosides **7–9**, which were not isolated pure, were ~10% The 1-nucleosides **1–3** were identical to the products synthesised by the indoline–indole method[7,8].



1 R = H
2 R = 5-NO_2
3 R = 6-NO_2



4 R = H, R′ = Ac
5 R = 5-NO_2, R′ = Ac
6 R = 6-NO_2, R′ = Ac
10 R = R′ = H
11 R = 5-NO_2 R′ = H
12 R = 6-NO_2, R′ = H



7 R = H R = Ac
8 R = 5-NO_2, R′ = Ac
9 R = 6-NO_2, R′ = Ac
13 R = R′ = H
14 R = 5-NO_2, R′ = H
15 R = 6-NO_2, R′ = H

Zemplén deacetylation of **4**, **5**, or **6** afforded the 1,2-*O*-ethylidene derivatives **10**, **11**, or **12**, respectively On treatment[9] with acetone–0 05M sulphuric acid, **5** or **6** did not change, but **11** or **12** gave traces (t l c) of 5- or 6-nitroindole, respectively. In acetone–5M sulphuric acid, each of these compounds gave the corresponding indole during 30 min 1-Arabinopyranosyl-6-nitroindole and its triacetate (**3**) were stable under these conditions

The p m r spectra of **4–6** and **10–12** contained singlets (δ 1 80–1 94) for methyl groups (Table II) The $^3J_{H,H}$ values for the carbohydrate protons of these compounds reflect distortion of the chair conformation similar to that observed in ortho esters of arabinopyranose[10]

The formation of *C*-nucleosides in the above reactions is noteworthy, as they were not obtained previously. *C*-Nucleosides **7–9** were deacetylated (Zemplén) to yield **13–15**, reacetylation (acetic anhydride–pyridine) regenerated **7–9**. Compounds **7–9** were partially decomposed during deacetylation, *cf* 1-(indol-3-yl)glycerol which, in the presence of alkali, gives indole and glyceraldehyde[11]

The structures of **7–9** were confirmed by spectroscopy The i r spectra contained bands characteristic of NH-stretching vibrations at 3360–3400 cm^{-1}. The signal (1 l p p m) for the NH proton in the p m r spectrum of **7** in $(CD_3)_2SO$ disappeared after exchange with D_2O. There were no H-3 doublets at δ 6 5 in the spectra of **7–9** and **13–15** (Table III), and the H-2 singlets were shifted downfield to the region of the H-7 and H-4 signals The value (9 6 Hz) of $J_{1,2}$ confirmed that H-1,2 were trans-diaxial and demonstrated the α-configuration and $^4C_1$ conformation of the pyranoid ring The c d spectra of the *C*- and *N*-nucleosides **9** and **3** showed positive Cotton effects at 355 (θ 7.6 × 10^3) and 330 nm (θ 2.5 × 10^3); **6** gave no definite maxima

TABLE II

P M R DATA FOR THE 1,2-*O*-INDOLYLETHYLIDENE DERIVATIVES OF L-ARABINOPYRANOSE

Compound	*Chemical shifts, p p m (Coupling constants, Hz)*													*Solvent*
	Indole protons						*Sugar protons*							
	H-7	*H-6*	*H-5*	*H-4*	*H-3*	*H-2*	*H-1* ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5b}$)	*H-5a* ($J_{4,5a}$)	*H-5b* ($J_{5a,5b}$)	*Ac Me*	
4	7 79			6 78[a]	6 37	[a]	5 42 (4 4)	4 06[b] (4 8)	5 38	5 15 (4 4)	4 11–3 90[b] (4 6)	3 62 (12 8)	1 92 1 87 1 80	$CDCl_3$[c]
5[d]	7 73	8 07		8 48	6.61	7 41	5 53 (4 6)	4 23 (4 0)	5 38 (5 6)	5 27 (4 4)	4 16 (4 1)	3 86 (12 5)	2 10 2 03 1 94	$CDCl_3$
6	8 67		8 00	7 60	6 57	7 53	5 57 (4 6)	4 25[b] (4 8)	5 55	5 30 (4 2)	4 35–4 08[b] (4 0)	3 83 (12 8)	2 09 2 03 1 91	$CDCl_3$
10	7 80			7 00	6 41	7 32	5 49 (3 2)	4 20		3 82 (6 2)	3 78	3 68 (10 6)	1 87	CD_3OD
11[d]	7 80	8 02		8 48	6 67	7 54	5 45 (3 7)	4 03 (4 0)	4 00 (4 4)	3 91 (5 6)	3 82 (4 0)	3 70 (11 6)	1 88	CD_3OD
12	8 54		7 93	7 75	6 67	7 81	5 00 (4 4)	4 10		3 50	5 51	5 28	1 90	$(CD_3)_2SO$

[a,b]Overlapping signals [c]Spectrum recorded at 50° [d]360-MHz spectrum recorded with a Bruker WH spectrometer

TABLE III

P.M R DATA FOR THE 3-α-L-ARABINOPYRANOSYL DERIVATIVES OF INDOLES

Compound	*Chemical shifts, p p m (Coupling constants, Hz)*											
	Indole protons					*Sugar protons*						
	H-7	*H-6*	*H-5*	*H-4*	*H-2*	*H-1* ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5b}$)	*H-5a* ($J_{4,5a}$)	*H-5b* ($J_{5a,5b}$)	*Ac*
7[b]	8 37				6 92	4 46 (9 6)	5 65 (10 0)	5 19 (3 6)	5 40 (0 8)	4 12 (2 0)	3 78 (13 2)	2 16 1 95 1 68
8[b]	7 40–7 20[a]	8 05		8 78	[a]	4 63 (9 6)	5 60 (10 0)	5 20 (3 6)	5 43 (0 8)	4 17 (2 0)	3 80 (13 2)	2 24 1 96 1 73
9[b]	9 27		8 17	7 75	7 77	4 62 (9 6)	5 52 (10 0)	5 19 (3 6)	5 42 (0 8)	4 15 (2 0)	3 84 (12 8)	2 19 1 97 1 76
13[c]	7 90				6 90	4 06 (9 6)	4 30 (9 2)	4 00 (3 6)	3 86	3 86 (1 6)	3 50 (12 8)	
14[c]	7 46	8 04		8 80	7 52	4 61					3 38	
15[c]	8 33		7 90[a]	[a]	7 65	4 65					3 77	

[a]Overlapping signals [b]In $CDCl_3$ [c]In CD_3OD

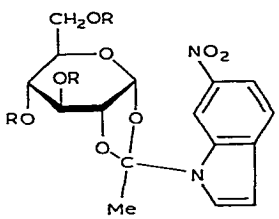
TABLE IV

P M R DATA FOR THE D-GLUCOSYL DERIVATIVES OF INDOLES

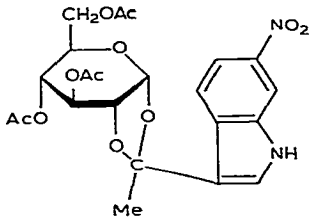
Compound	*Chemical shifts, p p m (Coupling constants, Hz)*												
	Indole protons						*Sugar protons*						
	H-7	*H-5*	*H-4*	*H-3*	*H-2*	*NH*	*H-1* ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5}$)	*H-5*	*H-6*	*Ac Me*
16[b]	8 66	7 98	7.60	6 54	7 50		5 74 (5 0)	[a] (2 4)	5 28 (2 4)	4 94 (9 2)	4 36——4 00[a]		2 16 2 12 2 03 2 00
17[b]	8 18	7.82	7 40		7 77	9 20	5 53 (5 0)	[a]	5 18	4 84	4 30——3 84[a]		2 08 2 06 1 96 1 90
18[c]	8 65	7 88	7 56	6 58	7 64		5 70 (5 0)	4 20———				3.44	1 95

[a]Overlapping signals [b]In $CDCl_3$ [c]In CD_3OD

The reaction of 6-nitroindole with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide yielded only the 1,2-*O*-ethylidene derivatives **16** and **17** in the ratio 3 1, pure **17** could not be isolated Deacetylation of **16** with methanolic ammonia gave 1,2-*O*-[1-(6-nitroindol-1-yl)ethylidene]-α-D-glucopyranose (**18**) Under these conditions, **17** gave 3-acetyl-6-nitroindole



16 R = Ac
18 R = H



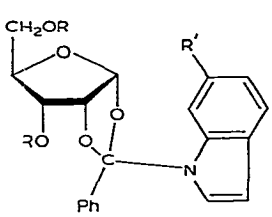
17

In the p m r spectra of **16–18**, the singlets (δ 1 9–2 0) at highest field correspond to ethylidene methyl groups The $J_{1\,2}$ values (5 Hz) are the same as for glucopyranose ortho esters[12] (Table IV) For **17**, the absence of a signal for indole H-3 was confirmed by the appearance of a sharp singlet for H-2 at low field The i r spectrum of **17** showed absorption for NH at 3360 cm^{-1} The c d spectrum of **16** contained a strong, negative extremum at 360 nm (θ 1 4 × 10^3)

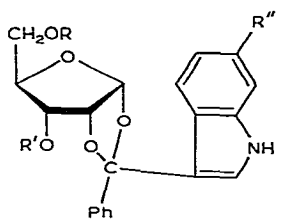
Treatment of **16** or **18** with acetone–5M sulphuric acid gave 6-nitroindole, **16** being the more stable Likewise, **17** yielded 3-acetyl-6-nitroindole

Dreiding models of the indolylethylidene derivatives of L-arabinose and D-glucose demonstrated that the configuration having the indole nucleus *exo* is the more probable

Whereas treatment of 6-nitroindole with 2,3,5-tri-*O*-acetyl-D-ribofuranosyl bromide did not afford any nucleoside derivatives, the reaction with 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl bromide gave a mixture of 3,5-di-*O*-benzoyl-1,2-*O*-[6-nitroindol-1-yl(phenyl)methylidene]-α-D-ribofuranose (**19**) and 3,5-di-*O*-benzoyl-1,2-



19 R = Bz R' = NO_2
21 R = Bz,R' = H
23 R = H,R = NO_2
24 R = H,R = H
25 R = Ac R' = NO_2



20 R = R' = Bz,R'' = NO_2
22 R = R' = Bz,R = H
26 R = Bz R = H,R' = NO_2
27 R = R' = R'' = H

TABLE V

P M R DATA FOR THE D-RIBOFURANOSYL DERIVATIVES OF INDOLES

Compound	*Chemical shifts, p p m (Coupling constants, Hz)*													
	Indole protons						*Sugar protons*							
	H-7	*H-6*	*H-5*	*H-4*	*H-3 (NH)*	*H-2*	*H-1* ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5b}$)	*H-5a* ($J_{4,5a}$)	*H-5b* ($J_{5a,5b}$)	*Ph*	*Bz Ac*
19[b]	8 44		8 20—7 20[a]		6 61	[a]	6 18 (4 0)	5 21 (5 2)	5 28——			4 40	7 31	[a]
20[b]	8 40——			7 20[a]	(9 46)	[a]	6 16 (3 8)	5 36——				4 35	[a]	[a]
21[b]	8 16——			6 83[a]	6 50	[a]	6 14 (4 0)	5 22—5 00		4 88——		4 32	7 31	[a]
23[c]	8 41		8 04—7 20[a]		6 70	[a]	6 06 (4 0)	4 66	4 20—4 04		3 91	3 62	7 31	
24[c]	7 64——			6 88[a]	6 53	[a]	5,97 (4 0)	4 62 (4 0)	4 20——			3 48	7 26	
25[b]	8 40		7 96	7 58	6 64	7 65	6 06 (4 2)	5 02 (5 0)	4 76 (5 0)	4 64—4 30 (5 3)	(2 0)	4.20 (12 6)	7 31	2 12 2 01
26[c]	8 32		8 20—7 20[a]			[a]	5,97 (4 0)	4 72—4 54		4 34	4 21	4 05	[a]	[a]
27[c]	8 31		7 82	7 28[a]		[a]	5 91 (4 0)	4 55 (4 0)	4 08—3 84 (4 4)		3 75 (1 2)	3 62	[a]	

[a]Overlapping signals [b]In $CDCl_3$ [c]In CD_3OD

O-[6-nitroindol-3-yl(phenyl)methylidene]-α-D-ribofuranose (**20**) in the ratio 4 1 In a parallel reaction, indole gave 3,5-di-*O*-benzoyl-1,2-*O*-[indol-1-yl(phenyl)-methylidene]-α-D-ribofuranose (**21**, 77%) and only traces of the 3-indolyl compound **22**

The properties of **19** and **21** are different from those of *O*-acylated 1-ribofuranosylindoles For example, the $J_{1,2}$ values[13] for indole nucleosides are 5 5–7 5 Hz, but the $J_{1,2}$ values for **19**, **21**, and its derivatives **23–25** are ~4 Hz (Table V) Debenzoylation of **19** or **21** with methanolic ammonia gave **23** or **24**, respectively, and acetylation of **23** yielded **25** The p m r spectrum of **25** revealed two acetyl singlets at high field and a singlet for phenyl protons at δ 7 31 (Table V) Treatment of **19**, **23**, or **25** with acetone–5M sulphuric acid gave 6-nitroindole Under these conditions, 6-nitro-1-β-D-ribofuranosylindole and its *O*-acylated derivatives were stable

Treatment of **20** with methanolic ammonia at 4° effected monodebenzoylation and gave **26** (*cf* ref 14), but 1,2-*O*-[6-nitroindol-3-yl(phenyl)methylidene]-α-D-ribofuranose **27** was formed at 25° The p m r spectra of **20**, **26**, and **27** contain no signals for H-3 (Table V) The i r spectra contain NH absorbances at 3360 cm^{-1} Treatment of **20** with acetone–10M sulphuric acid gave 3-benzoyl-6-nitroindole, the mass spectrum of which contained signals at *m/e* 266 (M^+), 189 (M^+ — Ph), 143 (M^+ — Ph — NO_2), 105 (PhCO), and 162 (B + 1) The c d spectrum of **19** showed negative and positive Cotton effects at 305 (θ 1 6 × 10^3) and 360 nm (θ 0 7 × 10^3), respectively

The electron-impact mass spectra of the *O*-acylated 1- and 3-indole nucleosides and the 1,2-*O*-(indol-1-yl)alkylidene and 1,2-*O*-(indol-3-yl)alkylidene derivatives were complex, showing low-intensity peaks for molecular ions The formulae of compounds **2**, **3**, **5**, **6**, **8**, **9**, **16**, **17**, **19**, **20**, **22**, and **25** were confirmed by high-resolution mass spectrometry Fragmentation of the carbohydrate–heterocycle bond leads to (S — X_1) and (B + 1 — X_2) peaks Peaks corresponding to *m/e* values of B + 28, B + 29, B + 30, and B + 43, as well as S and B + 1, are diagnostic The data in Table VI show that the fragmentation of the *N*-nucleosides **2** and **3** and the *C*-nucleoside **8** agrees with that obtained previously for compounds of similar type[15,16]. The fragmentation of the ethylidene–heterocycle bond in the ethylidene derivatives **5**, **6**, **16**, and **17** leads to peaks with *m/e* B + 43 For **17**, this peak is rather prominent, due to stabilisation through the six-membered structure **28** The lack of such stabilisation is the reason for the absence of peaks with *m/e* B + 28 and B + 29 in the mass spectra of **5**, **6**, and **16** This pattern appears to be general for 1,2-*O*-(indol-1-yl)-alkylidene derivatives of sugars which possess a heterocycle attached to the ethylidene

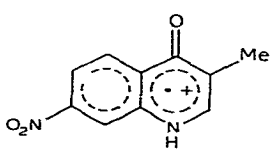


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TABLE VI

STRUCTURAL CORRELATIONS FOR DIAGNOSTIC IONS FROM THE MASS SPECTRA

Compound	*Relative intensities*					
	S	*B + 1*	*B + 28*	*B + 29*	*B + 30*	*B + 43*
2	100	3	13	—	—	9
3	100	20	—	17	—	6
5	100	17	—	—	—	4
6	100	14	—	—	—	1
8	100	—	20	14	100	10
16	100	33	—	—	—	3
17	100	18	8	—	—	40

moiety *via* an N–C bond Probably due to the tendency to eliminate benzoic acid, the differences in fragmentation pathways of **19** and **20** are not informative Many of the fragmentations suggested were supported by metastable peaks.

Atwood[4] reported that 4-nitro-1-β-D-ribofuranosylindole was obtained by treatment of 4-nitroindole with 2,3,5-tri-*O*-benzoylribofuranosyl bromide in the presence of Ag_2O and molecular sieve in benzene and subsequent debenzoylation However, analytical data, the instability in acids, and the $J_{1,2}$ value (4 5 Hz) suggest that this compound was 1,2-*O*-[4-nitroindol-1-yl(phenyl)methylidene]-α-D-ribofuranose

EXPERIMENTAL

General — P m r spectra (internal Me_4Si) were recorded with a Jeol JNM-MH-100 instrument at 30° I r spectra were recorded with a Perkin–Elmer 283 instrument C d spectra were determined for solutions in ethanol with a Mark-III Dichrograph Optical rotations were determined with a Perkin–Elmer 241 polarimeter T l c was performed on Silufol, and p l c on a mixture of silica gel AA_{254} 5/40 μm and silica gel *A* 40/100 μm, *O*-acetylated compounds were developed in carbon tetrachloride–acetone (4 1) Detection was effected, as appropriate, with u.v. light or with 5% *p*-dimethylaminobenzaldehyde in ethanolic hydrogen chloride (*N*-indole derivatives immediately gave red spots, and *C*-indole derivatives gave brown spots after heating) Substances were eluted from silica gel by methanol Mass spectra (80 eV) were obtained with a Varian MAT-311A instrument, samples were introduced directly at 100–200° with an accelerating voltage of 3 kV and an emission current of 3 mA

Condensations with 2,3,4-tri-O-acetyl-β-L-arabinopyranosyl bromide — (*a*) *With indole* A mixture of indole (234 mg), Ag_2O (464 mg), dry benzene (100 ml), and molecular sieve (Wolfen Zeosorb 4A Kugelform) was heated to reflux in a stream of nitrogen Solvent (~20 ml) was evaporated and a solution of glycosyl bromide

(1016 mg) in dry benzene (20 ml) was added dropwise during 2 5 h The mixture was boiled for 4 h with very slow distillation of solvent (~15 ml), cooled, and filtered, and the insoluble material was washed with benzene The combined filtrate and washings were concentrated and the residue was subjected to p l c , to give crude **7** (R_F 0 26), **1** (R_F 0 40, 110 mg, 14 7%), and crude **4** (R_F 0 47, ~20 mg).

Compound **1** had m p. 135–136° (from ethanol), $[\alpha]_D^{20}$ +51° (*c* 4, chloroform)[7].

(*b*) *With 5-nitroindole.* 5-Nitroindole (324 mg) was treated with Ag_2O (464 mg) and glycosyl bromide (1016 mg) as described in (*a*) Crystallisation of the product from ethanol gave **5** (270 mg) The material in the mother liquor was subjected to p l c to give more **5** (R_F 0 42, 62 mg, total yield 39 5%), **2** (R_F 0 32, 70 mg, 8 3%), and crude **8** (R_F 0 22)

Compound **2** had m p 162–164° (from xylene), $[\alpha]_D^{20}$ +25° (*c* 1, chloroform)[8]

(*c*) *With 6-nitroindole* The reaction of 6-nitroindole (324 mg), Ag_2O (464 mg), and glycosyl bromide (1016 mg), as described in (*a*), gave, after p l c , **6** (R_F 0 38, 340 mg, 40 4%), crude **9** (R_F 0 21) and **3** (R_F 0 29, 90 mg, 10 7%)

Compound **3** had m p. 157–158° (from xylene), $[\alpha]_D^{20}$ −44° (*c* 1, chloroform)[8]

*1,2-*O*-[1-(5-Nitroindol-1-yl)ethylidene]-β-*L*-arabinopyranose* (**11**) — To a solution of **5** (230 mg) in methanol (5 ml) was added methanolic 0 1M sodium methoxide, and the stirred reaction mixture was kept at 20° for 30 min, and then stirred with KU-2 (H^+) resin, filtered, and concentrated The residue was subjected to p l c with carbon tetrachloride–acetone (1 2), to give **11** (160 mg, 87 0%), R_F 0 58

*1,2-*O*-[1-(6-Nitroindol-1-yl)ethylidene]-β-*L*-arabinopyranose* (**12**) — Treatment of **6** (340 mg) as described above for **5** afforded a crude product which crystallised from ethanol to yield **12** (210 mg, 77 2%)

*3-α-*L*-Arabinopyranosylindole* (**13**) — To a solution of crude **7** (obtained from 234 mg of indole) in methanol (5 ml) was added methanolic 0 1M sodium methoxide (0 5 ml) The reaction mixture was treated as described for **11**, to give **13**, which was purified by p l c with carbon tetrachloride–acetone (1 2) The product (51 mg, 10 3%) had R_F 0 17

*3-α-*L*-Arabinopyranosyl-5-nitroindole* (**14**) — Similar treatment of crude **8** (obtained from 324 mg of 5-nitroindole) gave **14** (61 mg, 10 3%), R_F 0 17

*3-α-*L*-Arabinopyranosyl-6-nitroindole* (**15**) — Similar treatment of crude **9** (obtained from 324 mg of 6-nitroindole) gave **15** (77 mg, 12 9%), R_F 0 15, as yellow needles from methanol

*3-(2,3,4-Tri-*O*-acetyl-α-*L*-arabinopyranosyl)indole* (**7**) — Acetylation of **13** (30 mg) in pyridine (15 ml) with acetic anhydride (1 ml), followed by concentration and p l c of the residue, gave **7** (36 mg, 79 6%)

*5-Nitro-3-(2,3,4-tri-*O*-acetyl-α-*L*-arabinopyranosyl)indole* (**8**) — Acetylation of **14** (30 mg) gave **8** (28 mg, 65 1%)

*6-Nitro-3-(2,3,4-tri-*O*-acetyl-α-*L*-arabinopyranosyl)indole* (**9**) — Acetylation of **15** (30 mg) yielded **9** (34 mg, 77 3%)

*Reaction of 6-nitroindole and 2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl bromide* — The reaction of 6-nitroindole (162 mg), Ag_2O (232 mg), and glycosyl bromide

(617 mg), as described above, followed by p l c, gave two products (**16** and **17**) That (**16**) with R_F 0 42 was crystallised from chloroform–methanol to yield **16** (270 mg, 54 8%) A solution of crude **17** (R_F 0 25) in methanolic ammonia (5 ml) was kept at room temperature for 12 h Evaporation of the solvent and trituration of the residue with chloroform and methanol gave 3-acetyl-6-nitroindole (35 mg, 17 1%), ν_{max} 1636, 1619 [CO, C(2)=C(3)], and 3108 cm^{-1} (NH) Mass spectrum *m/e* 204 (M^+), 189 (M^+ — Me), and 143 (M^+ — Me — NO_2).

Anal Calc for $C_{10}H_8N_2O_3$ 0 5H_2O C, 56 3, H, 4 3, N, 13 1 Found C, 56 5, H, 4 2, N, 13 1

1,2-O-[1-(6-Nitroindol-1-yl)ethylidene]-α-D-glucopyranose (**18**) — A solution of **16** (90 mg) in methanolic ammonia (5 ml) was kept at room temperature for 12 h and then concentrated, and the residue was subjected to p l c with carbon tetrachloride–acetone (3 1). Further chromatography of the major product in carbon tetrachloride–acetone (1 2) gave **18** (62 mg, 87 3%), R_F 0 69

Reactions of 2,3,4-tri-O-benzoyl-D-ribofuranosyl bromide. — (*a*) *With 6-nitroindole* 6-Nitroindole (324 mg), glycosyl bromide (obtained from 1 512 g of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-D-ribofuranose), and Ag_2O (464 mg) were treated as described above, to give **19** (R_F 0 50, 960 mg, 79 1%) and crude **20** (R_F 0 34, 240 mg)

(*b*) *With indole* The reaction of indole (117 mg), glycosyl bromide (obtained from 756 mg of precursor), and Ag_2O (232 mg), as described above, gave **21** (430 mg, 76 6%), R_F 0 46

1,2-O-[6-Nitroindol-1-yl(phenyl)methylidene]-α-D-ribofuranose (**23**) — Deacetylation of **19** (620 mg) with methanolic ammonia (10 ml), as described for **18**, gave, after p l c (carbon tetrachloride–acetone, 2 1), **23** (220 mg), R_F 0 38

1,2-O-[Indol-1-yl(phenyl)methylidene]-α-D-ribofuranose (**24**) — Debenzoylation of **21** (200 mg) with methanolic ammonia (5 ml), as described for **18**, gave, after p l c. (carbon tetrachloride–acetone, 2 1), **24** (90 mg, 68 9%), R_F 0 13

5-O-Benzoyl-1,2-O-[6-nitroindol-3-yl(phenyl)methylidene]-α-D-ribofuranose (**26**) — A solution of crude **20** (270 mg) in methanolic ammonia (5 ml) was kept at 4° overnight Work-up as described for **18** with p l c (carbon tetrachloride–acetone, 2·1) of the product, gave **26** (60 mg, 5 9% yield from 6-nitroindole), R_F 0.50.

1,2-O-[6-Nitroindol-3-yl(phenyl)methylidene]-α-D-ribofuranose (**27**) — Debenzoylation of crude **20** (530 mg) at room temperature gave **27** (210 mg, 28 2%), R_F 0 18

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