SYNTHESIS AND STUDY OF L-ARABINOPYRANOSIDES OF 5- AND 6-NITROINDOLES

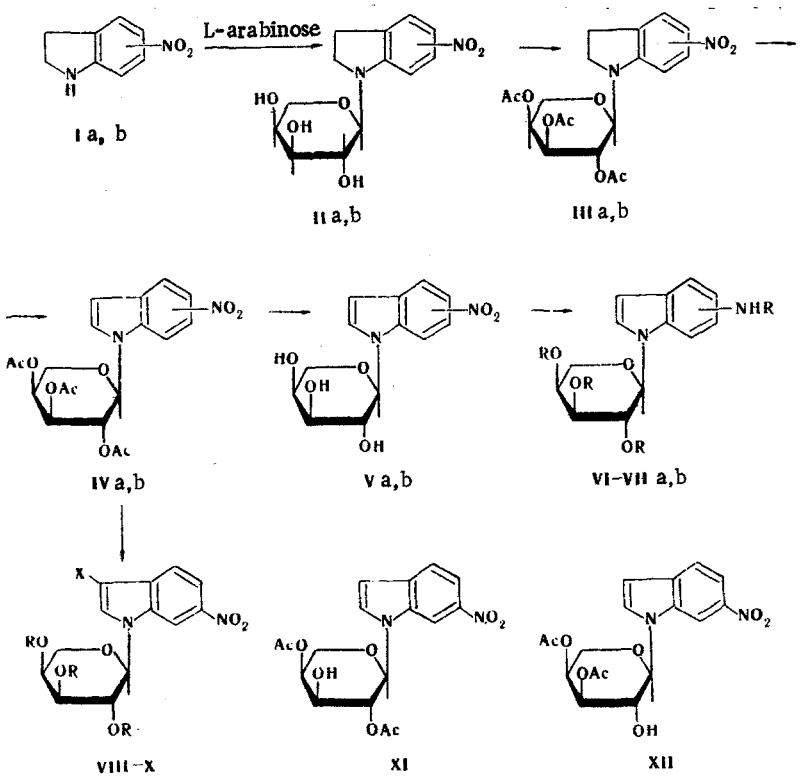
V. I. Mukhanov, I. V. Yartseva,
L. V. Éktova, N. D. Chkanikov,
T. D. Miniker, and M. N. Preobrazhenskaya

UDC 547.751+455.522

Condensation of 5- or 6-nitroindoline with L-arabinose gave 1-α-L-arabinopyranosyl-5 (or 6)-nitroindolines, which, after acetylation, dehydrogenation, and removal of the protective groups, are converted to 1-α-L-arabinopyranosyl-5(or 6)-nitroindoles and then to the corresponding amino derivatives. 1-α-L-Arabinopyranosyl-6-nitro-3-bromo-(iodo)indoles were obtained. The selective 2'-O- and 3'-O-deacetylation of 1-(2', 3', 4'-tri-O-acetyl)-α-L-arabinopyranosyl-6-nitroindole was accomplished.

Antitumorigenic activity was detected in experiments with animal L-arabinopyranosides of indole during a systematic study of nucleosides of indoles [1]. The aim of the present research was to study L-arabinopyranosides of 5- and 6-nitroindole and their derivatives. The most convenient method for the preparation of indole glycosides is the indoline—indole method, the first step of which consists in the preparation of 1-glycosides of substituted indolines [2].

1-α-L-Arabinopyranosyl-5(or 6)-nitroindolines IIa, b, respectively, were obtained in 88-90% yields by heating 5(or 6)-nitroindoline Ia or Ib with L-arabinose in aqueous alcohol in the presence of acetic acid and subsequent chromatographic purification. Acetylation of arabinosides IIa, b with acetic anhydride in pyridine led to 1-(2',3',4'-tri-O-acetyl)-α-L-arabinopyranosyl-5(or 6)-nitroindolines IIIa, b (in 90-95% yields). The dehydrogenation



Compounds I—VII: a — 5-substituted, b — 6-substituted; VIa, b R = H; VIIa, b R = Ac; VIII X=I, R=Ac; IX X=Br, R=Ac; X X=Br, R=H

Oncological Science Center, Academy of Medical Sciences of the USSR, Moscow 115478.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 224-229, February, 1979.
Original article submitted February 13, 1978.

 0009-3122/79/1502-

TABLE 1. Properties of the Compounds Obtained

Compound	mp, °C	Specific rotation, $[\alpha]_D^{20}$ (c, $CHCl_3$)	UV spectrum (in alcohol), λ_{max} (log ε)	Found, %			Empirical formula	Calculated, %		
				C	H	N		C	H	N
IIa	176—177	+151,0 (0,2[a])		52,5	5,5	10,0	$C_{13}H_{16}N_2O_6$	52,7	5,4	9,5
IIb	—[b]	+12,5 (0,2[a])	254 (4,08)	52,4	5,3	9,9	$C_{13}H_{16}N_2O_6$	52,7	5,4	9,5
IIIa	160—161	+150,0 (1,0)	227 (3,75)	54,0	5,3	6,6	$C_{19}H_{22}N_2O_9$	54,0	5,3	6,6
IIIb	—[b]	+62,0 (1,0)	252 (4,18), 360 (3,22)	54,1	5,4	6,8	$C_{19}H_{22}N_2O_9$	54,0	5,3	6,6
IVa	162—164	+25,0 (1,0)	264 (4,35), 313 (3,76)	54,4	4,9	6,9	$C_{19}H_{20}N_2O_9$	54,3	4,8	6,7
IVb	157—158	−44,0 (1,0)	246 (4,03), 317 (3,95), 350 (3,84)	54,2	4,9	6,7	$C_{19}H_{20}N_2O_9$	54,3	4,8	6,7
Va	210—212	+44,0 (1.0[c])	267 (4,15), 317 (3,76)	53,1	4,9	9,4	$C_{13}H_{14}N_2O_6$	53,1	4,8	9,5
Vb	192—193	+47,3 (1.5[c])	247 (4,28), 320 (3,96), 355 (3,90)	53,0	4,8	9,2	$C_{13}H_{14}N_2O_6$	53,1	4,8	9,5
VIIa	—[b]	+8,0 (1.0[c])	263 (4,17), 313 (3,76)	58,2	5,5	6,5	$C_{21}H_{24}N_2O_8$	58,3	5,6	6,5
VIIb	—[b]	+23,0 (1.2[c])	235 (4,38), 279 (4,08), 300 (3,73)sh	58,1	5,5	6,7	$C_{21}H_{24}N_2O_8$	58,3	5,6	6,5
VIII	185—187	—[d]	264 (4,41), 311 (3,88), 361 (3,71)							
IX	176—177	+4,6 (0,8)	262 (3, 89), 310 (3,75), 362 (3,60)			5,6	$C_{19}H_{19}BrN_2O_9$			5,6
X	147—149	+36,8 (0,9)	263 (3,81), 313 (3,89), 361 (3,56)	41,6	4,1 21,4	7,6 (Br)	$C_{19}H_{19}BrN_2O_9$	41,6	3,5 21,4	7,5 (Br)
XI	187—188	+36,0 (1,0)	248 (3,92), 318 (3,87), 360 (3,72)	53,5	5,0	7,9	$C_{17}H_{18}N_2O_8$	54,0	4,8	7,4
XII	178—180	−67,0 (1,0)	250 (3,94), 318 (3,81), 360 (3,73)	53,8	4,9		$C_{17}H_{18}N_2O_8$	54,0	4,8	

[a]Acetone. [b]An amorphous substance. [c]Methanol. [d]Could not be determined because of the intense color of the solution.

of indoline derivatives IIIa, b was accomplished with manganese dioxide. Nitroindole derivatives IVa, b were obtained in analytically pure form in 60-66% yields, and their deacetylation with sodium methoxide in methanol gave 1-α-L-arabinopyranosides of 5- or 6-nitroindole (Va, b) in 94.5 and 87% yields, respectively. Nitro derivatives Va, b were reduced by the action of hydrazine hydrate in the presence of Raney nickel to amino derivatives VIIa, b, were characterized additionally by tetraacetates VIIa, b, which were obtained in 63 and 82% yields, respectively, by acetylation of VIa, b with acetic anhydride in pyridine. The properties of the compounds obtained are presented in Table 1.

The confirmation of the structures of indole glycosides II-VII follows from an examination of the PMR spectra of these compounds (Table 2). The spin—spin coupling constant (SSCC) of the anomeric protons of II-VII is 9 Hz. This indicates a trans-diaxial orientation of the protons attached to the C-1' and C-2' atoms of the carbohydrate ring, which is possible only in the case of an α configuration and a $^4C_1$ conformation.

It seemed of interest to study the possibility of the transition from 6-nitroindole l-arabinopyranoside IVb to other derivatives with modified and carbohydrate rings. It is known that cleavage of the pyrrole ring occurs in the reaction of periodic acid or its salts with indoles, and instances of the iodination of compounds by the action of periodic acid have been described [3, 4].

1-(2',3',4'Tri-O-acetyl)-α-L-arabinopyranosyl-3-iodo-6-nitroindole VIII, which was isolated by chromatography, was obtained in 30.7% yield by the reaction of IVb with periodic acid in acetic anhydride.

A comparison of the PMR spectra of IVb and VIII shows that the signal of the proton attached to C-3 for VIII vanishes, whereas the signal of the proton attached to C-2 (a doublet at δ 7.54 for IVb) retained its position (δ 7.56) but degenerated to a singlet due to the absence of splitting with C_3—H. The mass spectrum contains a molecular-ion peak (m/e 546+)

TABLE 2. PMR Spectra of II-XII

Compound	Chemical shifts (δ, ppm), character of the signal, and SSCC (Hz)													Solvent, 25°C
	7-H, d ($J_{7,6}$)	6-H, dd ($J_{6,4}$)[a]	5-H, dd ($J_{5,7}$)[a]	4-H, d ($J_{4,5}$)	3-H, d ($J_{3,2}$)	2-H	1′-H, d ($J_{1',2'}$)	2′-H, ($J_{2',3'}$)	3′-H, dd ($J_{3',4'}$)	4′-H, m	5′-H, dd ($J_{5',5''}$) ($J_{5',4'}$)	5″-H, dd ($J_{5'',4''}$)	CH_3CO, s	
IIa	6,80 (9,0)	8,10	—	7,84	2,76 m	—[b]	5,06	4,60 t	4,40 — 3,70 m[b]				—	C_5D_5N
IIb	7,72	—	7,58	6,97 (7,6)	2,75 m	—[b]	5,12	4,62t	4,00 — 3,60 m[b]				—	C_5D_5N
IIIa	6,60 (9,0)	8,08	—	7,96	3,10 m	—[b]	4,97	5,54 q	5,22 (3,0)	5,38	4,20—3,70 m[b]		1,96, 2,04, 2,20	$CDCl_3$
IIIb	7,43	—	7,63	7,15 (9,0)	3,07	—[b]	4,93	5,53 q (9,5)	5,23 (3,5)	5,37	4,08—3,60 m[b]		2,01, 2,05, 2,20	$CDCl_3$
IVa	7,60 (9,5)	8,19	—	8,60	6,75 (3,5)	7,44 d	5,48	5,76 t	5,30 (3,5)	5,48	4,28 (13,5) (2,0)	3,96 (1,0)	1,68, 2,02, 2,27	$CDCl_3$
IVb	8,61 (1,5)	—	8,08	7,64 (9,0)	6,61 (3,5)	7,44 d	5,47	5,84 q (9,8)	5,30 (3,5)	5,47	4,28 (13,5) (2,0)	3,95 (1,0)	1,75, 2,04, 2,36	$CDCl_3$
Va	7,75 (9,0)	8,08	—	8,54 (3,5)	6,76	7,64 d	5,31	4,22 t	3,73 (3,0)	4,02 — 3,82 m				CD_3OD[c]
Vb	8,67 (1,5)	—	7,98	7,69 (9,0)	6,69 (3,5)	7,82 d	5,46	4,21 t	4,10 — 3,60 m					CD_3OD
VIa	7,20 (9,0)	6,55	—	6,76	6,16 (3,0)	7,14 d	5,00	4,16 t	4,00 — 3,30 m					CD_3OD
VIb	7,00	—	6,70 (1,7)	7,46	6,52 (3,0)	7,28 d	5,28	4,40 — 3,30 m						D_2O
VIIa	7,60 — 7,10 m[b]				6,28 (3,0)	—[b]	5,28	5,55 t	5,10 (3,5)	5,28	4,00 (13,5) (2,0)	3,72 (1,0)	1,60, 1,94, 2,06, 2,16	$CDCl_3$
VIIb	8,00	—	6,70 (1,6)	7,28	6,36 (3,0)	7,10 d	5,24	5,56 t	5,12 (3,0)	5,24	3,92 (13,0) (1,5)	3,66 (0,8)	1,64, 1,94, 2,08, 2,16	$CDCl_3$
VIII	8,60	—	8,12	7,50	—	7,56 s	5,52	5,72 t	5,32 (3,0)	5,52	4,28 (13,0) (2,0)	4,00 (0,8)	1,78, 2,05, 2,38	$CDCl_3$
IX[d]	8,56	—	8,00	7,50	—	7,36 s	5,37	5,74	5,27	5,37	4,18 (13,2) (2,0)	3,87 (0,8)	1,70, 1,94, 2,23	$CDCl_3$
X[d]	8,50	—	7,87	7,40	—	7,73 s	5,40 — 3,15 m							CD_3OD
XI	8,54	—	8,04	7,62	6,61 (3,0)	7,47 d	5,41 (9,2)	5,59 t (9,2)	4,48 (3,2)	5,28	4,32 (14,0) (2,0)	3,98 (0,8)	1,78, 2,34	$CDCl_3$
XII	8,62	—	8,04	7,66	6,61 (3,0)	7,52 d	5,32 (8,8)	4,53 q (9,2)	5,12 (3,2)	5,44	4,25 (13,6) (2,5)	3,88 (1,2)	2,08, 2,34	$CDCl_3$

[a] $J_{6,4} = J_{5,7} = 2.0$ Hz, $J_{4,5} = 8.0$ Hz, and $J_{1',2'} = J_{2',3'} = 9.0$ Hz in all cases except those noted in the table. [b] The signals are overlapped. [c] The spectrum was recorded at 60°C. [d] The spectra were recorded with a Bruker WP-60 spectrometer.

and fragment peaks of iodonitroindole (m/e 287^+) and sugar (m/e 259^+) residues. It may be assumed that iodine enters the 3 position. It is known that the iodination of indole with iodine leads to the formation of 3-iodoindole [5]. In addition, the electrophilic substitution reactions of 1-(2',3',4',5'-tetra-O-acetyl)-β-D-glucopyranosylindole lead to the formation of 3-substituted indoles [6].

1-(2',3',4'-Tri-O-acetyl)-α-L-arabinopyranosyl-3-bromo-6-nitroindole (IX) was obtained in 96% yield by direct bromination of IVb in chloroform at room temperature. The UV spectrum of IX is similar to the UV spectrum of VIII. The PMR spectrum does not contain the signal of a pyrrole proton at 6.6 ppm, but the mass spectrum contains a molecular-ion peak (m/e 499^+) and fragment peaks of bromonitroindole (m/e 240^+) and sugar (m/e 259^+) residues. The peaks of the fragments that contain bromine have the characteristic isotope distribution.

Crystalline 1-α-L-arabinopyranosyl-3-bromo-6-nitroindole (X) was obtained in 91% yield after removal of the acetate groups with sodium methoxide and chromatographic purification.

In order to study the possibility of the preparation of derivatives with modified sugar residues we investigated the selective deacetylation of 1-(2',3',4'-tri-O-acetyl)-α-L-arabinopyranosyl-6-nitroindole (IVb). A mixture of mono- and dideacetylated nucleosides in which 2',4'-di-O- and 3',4'-di-O-acetyl derivatives XI and XII predominate can be obtained by the action of mineral acids ($HClO_4$, HIO_4 or HCl) in aqueous methanol. Thus 38.8% XI and 10% XII were isolated in the reaction of $HClO_4$ in aqueous methanol at 50°C with IVb. In the PMR spectra the signals of the protons attached to 3-C in XI and 2-C in XII are shifted to strong field as compared with the corresponding protons of IVb; this confirms the structures of the partially deacetylated derivatives XI and XII. The mass spectra of XI and XII contains molecular-ion peaks and fragment peaks of nitroindole and carbohydrate residues (m/e 378^+, 161^+, and 217^+).

Compounds XI and XII can be used for the preparation of the corresponding phosphates.

EXPERIMENTAL

The mass spectra were recorded with an LKV-9000 spectrometer, the PMR spectra were recorded with a JNM-MH-100 spectrometer with tetramethylsilane as the internal standard, the IR spectra were recorded with a UR-10 spectrometer, and the UV spectra were obtained with a Unicam SP-800 spectrophotometer. The specific rotation was measured with a Perkin–Elmer 241 spectrometer. Column chromatography was accomplished with L 40/100μ silica gel, and thin-layer chromatography (TLC) was accomplished with LSL_{254} 5/40μ silica gel on 18 by 18-cm plates (the thickness of the loose layer was 1 mm). The course of the reactions and the purity of the compounds obtained were monitored by means of TLC on Silufol UV-254. Mixtures of benzene with acetone with solvent ratios of 1 : 2 (A), 1 : 1 (B), 1.4 : 1 (C), 4 : 1 (D), and 6 : 1 (E) were used as the eluents. The chromatograms were developed in UV light and with Erlich's reagent (a 5% solution). The solutions were evaporated in vacuo at 40-45°C.

1-α-L-Arabinopyranosyl-5-nitroindoline (IIa). A mixture of 7.8 g (47.5 mmole) of 5-nitroindoline (Ia) [7], 5 g (33.4 mmole) of L-arabinose, 2.5 ml of acetic acid, 25 ml of water, and 125 ml of ethanol was stirred at 50°C for 4 h, after which it was evaporated to dryness, and the residue was recrystallized from methanol. The crystals were removed by filtration to give 5 g (50.7%) of arabinoside IIa. The mother liquor was evaporated to dryness, and the residue was chromatographed with a 6 by 10-cm column (elution with mixture B). Evaporation of the fractions containing arabinoside IIa gave an additional 3.7 g (37.5%) of IIa with R_f 0.35 (system A).

1-(2',3',4'-Tri-O-acetyl)-α-L-arabinopyranosyl-5-nitroindoline (IIIa). A 10-g (33.6 mmole) sample of arabinoside IIa was dissolved in 80 ml of pyridine, 72 ml of acetic anhydride was added with stirring at 0-5°C, and the mixture was allowed to stand overnight at 20°C. It was then poured over ice, and the crystals were removed by filtration, washed with water, and air dried to give 13.6 g (95.7%) of triacetyl derivative IIIa with R_f 0.10 (system C). According to the data in [8], this compound has mp 152-154°C.

1-α-L-Arabinopyranosyl-6-nitroindoline (IIb) and 1-(2',3',4'-Tri-O-acetyl)-α-L-arabinopyranosyl-6-nitroindoline (IIIb). A mixture of 78 g (47.5 mmole) of 6-nitroindoline (Ib) [7], 50 g (334 mmole) of L-arabinose, 25 ml of acetic acid, 250 ml of water, and 1250 ml of ethanol, was stirred at 50°C for 4 h, after which it was evaporated to dryness. The residue was used in the acetylation reaction. To obtain an analytically pure sample, 128 mg of the residue

was dissolved in 1 ml of acetone and chromatographed on a plate in system C. The product was eluted with acetone, and the eluate was evaporated to dryness to give 92.6 mg (90%) of arabinoside IIb as an amorphous orange substance with R_f 0.10 (system C). The bulk of the dry residue (∿ 122 g) was dissolved in 1 liter of pyridine, 900 ml of acetic anhydride was added with stirring to the solution at 0-5°C, and the mixture was allowed to stand overnight at 20°C. It was then poured over 5 kg of crushed ice, and the precipitate was removed by filtration, washed with water, and dried to give 169 g of crude triacetyl derivative IIIb.

To obtain an analytically pure sample, 110 mg of crude triacetate IIIb was dissolved in 1 ml of chloroform and chromatographed on a plate in system D. The product was eluted with acetone, and the eluate was evaporated to dryness to give 74 mg (90.0%) of analytically pure IIIb as an amorphous substance with R_f 0.60 (system D).

1-(2',3',4'-Tri-O-acetyl)-α-L-arabinopyranosyl-5-nitroindole (IVa). A 10-g (23.6 mmole) sample of triacetyl derivative IIIa was dissolved in 150 ml of absolute benzene, 40 g of active MnO_2 was added, and the mixture was refluxed with stirring and azeotropic removal of the water by distillation for 12 h. The precipitate was removed by filtration and washed with chloroform. The filtrate was evaporated to dryness, and the residue was recrystallized from xylene to give 5.95 g (60.0%) of indole derivative IVa with R_f 0.50 (system D).

1-(2',3',4'-Tri-O-acetyl)-α-L-arabinopyranosyl-6-nitroindole (IVb). This compound, with R_f 0.45 (system D), was obtained in 66.3% yield from crude triacetyl derivative IIIb by the method presented above for IVa.

1-α-L-Arabinopyranosyl-5-nitroindole (Va). A 6-g (14.3 mmole) sample of triacetate IVa was suspended in 60 ml of absolute methanol, a solution of sodium methoxide in methanol (15 mg of sodium in 7 ml of methanol) was added, and the solution was stirred for 1 h. The precipitated crystals were removed by filtration, washed with methanol, and dried in vacuo to give 2 g (47.5%) of nucleoside Va. Ion-exchange resin (KU-2) was added to the filtrate with stirring up to pH 7, and the resin was removed by filtration. The filtrate was evaporated to a volume of 7 ml and allowed to stand at 5°C for 18 h. The precipitated crystals were removed by filtration, washed with methanol, and dried in vacuo to give an additional 1.97 g (47.0%) of 5-nitroindole derivative Va with R_f 0.42 (system A).

1-α-L-Arabinopyranosyl-6-nitroindole (Vb). This compound, with R_f 0.46 (system A), was obtained in 87.0% yield from triacetyl derivative IVb by a method similar to that used to obtain arabinoside Va.

1-(2',3',4'-Tri-O-acetyl)-α-L-arabinopyranosyl-5-acetamidoindole (VIIa). A 0.5-g sample of 1-α-L-arabinopyranosyl-5-nitroindole (Va) was dissolved in 40 ml of methanol, 1 g of Raney nickel was added, and 2 ml of hydrazine hydrate was added at room temperature in the course of 10 min. The mixture was stirred for 1 h, and the precipitate was removed by filtration. The filtrate was evaporated to dryness, and a fifth of the dry residue was chromatographed on a plate in system A. The fraction with R_f 0.14 was collected and eluted with methanol. The eluate was evaporated to dryness to give 0.05 g (55.5%) of 1-α-L-arabinopyranosyl-5-aminoindole (VIa). The remaining dry residue was dissolved in 5 ml of pyridine, 5 ml of acetic anhydride was added, and the mixture was allowed to stand at 20°C for 15 h. The residual acetic anhydride and pyridine were removed in vacuo, and the residue was dissolved in 5 ml of chloroform and chromatographed on five plates in system B. The product was eluted with chloroform, and the eluate was evaporated to dryness to give 0.37 g (63.4%) of acetamido derivative VIIa with R_f 0.50 (system B).

1-α-L-Arabinopyranosyl-6-aminoindole (VIb) and 1-(2',3',4'-Tri-O-acetyl)-α-L-arabinopyranosyl-6-acetamidoindole (VIIb). These compounds, with R_f 0.14 (system A) and Rf 0.50 (system B), were obtained in 57.6 and 82.3% yields, respectively, by a method similar to that used to prepare arabinopyranosides VIa and VIIa.

1-(2',3',4'-Tri-O-acetyl)-α-L-arabinopyranosyl-3-iodo-6-nitroindole (VIII). A solution of 0.5 g (2.6 mmole) of HIO_4 in 15 ml of acetic anhydride was added in the dark to a solution of 0.5 g (1.2 mmole) of acetate IVb in 3 ml of acetic anhydride, and the mixture was allowed to stand for 1 h. It was then poured into 150 ml of ice water, and the aqueous mixture was allowed to stand at 20°C for 5 h. It was then extracted with 20 ml of chloroform, and the extract was dried with Na_2SO_4. The solvent was removed by distillation, and the residue was chromatographed on plates in system E. The product was extracted with acetone, the solvent was removed by distillation, and the residue was dried in vacuo to give 0.2 g (30.7%) of yellow crystals of iodo derivative VIII with R_f 0.37 (system E).

1-(2',3',4'-Tri-O-acetyl)-α-L-arabinopyranosyl-3-bromo-6-nitroindole (IX). A solution of 6.2 g (39 mmole) of Br_2 in 100 ml of chloroform was added to a solution of 2 g (4.8 mmole) of acetate IVb in 250 ml of chloroform, and the mixture was stirred for 1 h. The solvent was removed by distillation, the residue was dissolved in 50 ml of chloroform, and the solvent was removed completely by distillation. The latter operation was repeated three times. The residue was recrystallized from methanol, and the yellow crystals were dried in vacuo to give 2.3 g (96.0%) of 3-bromo-6-nitroindole derivative IX with R_f 0.34 (system E).

1-α-L-Arabinopyranosyl-3-bromo-6-nitroindole (X). A 3-ml sample of a 0.1 N solution methoxide in methanol was added to a suspension of 2 g (4 mmole) of bromo derivative IX in 200 ml of absolute methanol. After 1 h, the reaction mixture was neutralized to pH 7 with KU-2 resin. The resin was removed by filtration, and the filtrate was evaporated to dryness to give 1.54 g (91.0%) of 3-bromo-6-nitroindole derivative X in the form of a yellow crystalline substance. An analytically pure sample (R_f 0.35) was obtained after chromatography of 0.1 g of the dry residue on plates in a chloroform—methanol system (4 : 1).

1-(2',4'-Di-O-acetyl)-(XI) and 1-(3',4'-Di-O-acetyl)-α-L-arabinopyranosyl-6-nitroindole (XII). A solution of 10.6 g (102 mmole) of $HClO_4$ in 225 ml of water was added to a solution of 1.0 g (2.4 mmole) of acetate IVb in 450 ml of methanol, and the mixture was heated at 50°C for 16 h. It was then cooled and extracted with chloroform (50 ml), and the extract was washed with water and dried with $MgSO_4$. The solvent was removed in vacuo, and the residue was chromatographed on plates with silica gel in system D. The product was eluted with acetone, the eluate was evaporated to dryness, and the residue was dried in vacuo to give 0.34 g (38.8%) of 2',4'-di-O-acetate XI and 0.09 g (10.0%) of 3',4'-di-O-acetate XII with R_f values of 0.15 and 0.27 (system D), respectively.

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