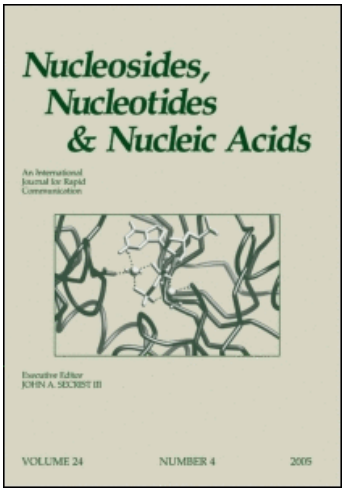

Nucleosides, Nucleotides and Nucleic Acids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597286

The Reaction of D-Arabinopyranosylurea with Malononitrile and Triethyl Orthoformate

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To cite this Article Stankevich, E. , Dreimane, A. , Liepinš, E. , Kemme, A. and Bleidelis, J.(1983) 'The Reaction of D-Arabinopyranosylurea with Malononitrile and Triethyl Orthoformate', Nucleosides, Nucleotides and Nucleic Acids, 2: 2, 155 — 173
To link to this Article: DOI: 10.1080/07328318308081256
URL: http://dx.doi.org/10.1080/07328318308081256

NUCLEOSIDES & NUCLEOTIDES, 2(2), 155-173 (1983)

THE REACTION OF D-ARABINOPYRANOSYLUREA WITH MALONONITRILE AND TRIETHYL ORTHOFORMATE

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ABSTRACT

Three-component coupling of arabinosylurea (or its triacetyl derivative), malononitrile and triethyl orthoformate affords 1-(α-D-arabinopyranosyl)-ureidomethylenemalononitriles. These compounds in the presence of triethylamine undergo cyclization to give 2-oxo-4-imino-5-cyano-3-(α-D-arabinopyranosyl)-2,3,4,5-tetrahydropyrimidines. The pyranose structure of arabinosylurea was demonstrated by X-ray analysis. The synthesized compounds were studied by ^{1}H, ^{13}C NMR spectroscopy.

The biological activity possessed by 1-ß-D-arabinofuranosylcytosine has stimulated the development of synthetic methods leading to arabinosylpyrimidines. Apart from the classical methods of synthesis where arabinosylpyrimidines are obtained from sugars and pyrimidine bases or by the modification of the sugar or pyrimidine moiety in the nucleoside molecule [1], other methods are also available. 1-D-Arabinosylthymine synthesis from

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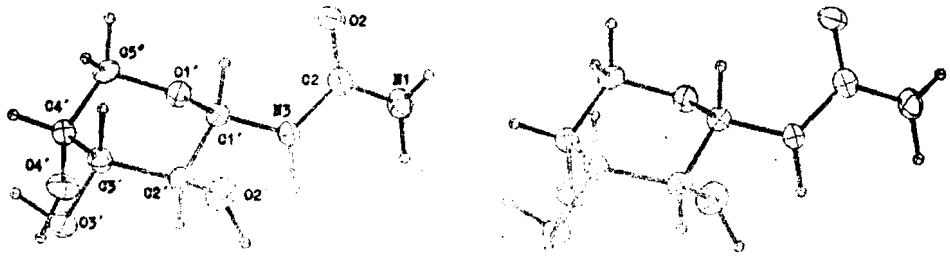
2',3',4'-tri-O-acetyl-D-arabinopyranosylurea and 2-methyl-3-methoxyacryloylchloride [2] has been described. 2,2'-Anhydronucleosides are readily convertible to arabinosylnucleosides and can be obtained from ß-D-arabinofurano-(1',2': 4,5)-2-oxazoline and acetylene derivatives [3,4]. We devised a method for arabinosylpyrimidine synthesis based on the research of Whitehead [5], who has shown that N-alkylureas are capable of reacting with malononitrile and orthoformate to yield N-alkyl-5-cyanocytosines.

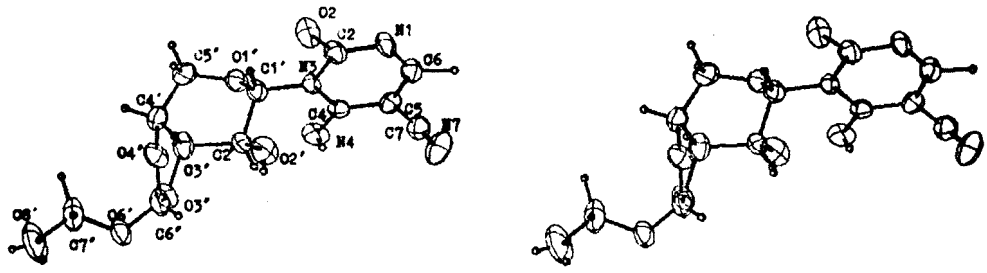
RESULTS AND DISCUSSION

Both unprotected arabinosylurea 1a [6] and 2',3',4'-triacetylarabinopyranosylurea 1b [2] were used as starting material. Arabinosylurea 1a was presumed to exist in the pyranose form [2,7]. However, the ^1H NMR spectra failed to give unequivocal results, since the $J_{1',2'} = 5.8$ Hz is rather low for the pyranose form [8].

For geometrical and conformational assignment of the carbohydrate moiety in arabinosylurea we undertook an X-ray analysis of compound 1a crystallizable in the form of colorless paralellepipeds with monoclinic system, its composition being $C_6H_{12}O_5N_2 \cdot H_2O$. It is apparent from the stereoview of 1a molecule (Fig.) that the compound corresponds to α-D-arabinopyranosylurea. The 6-membered cycle is characterized by a somewhat distorted flattened chair conformation $^1C_4$ with equatorially lo-



1a



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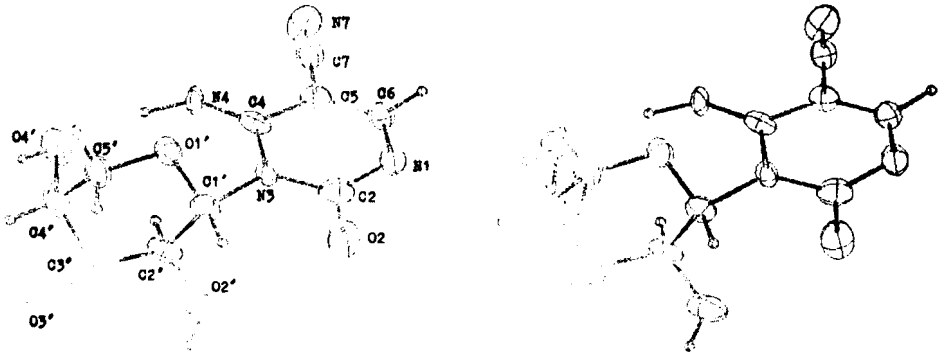


7

cated nonhydrogen substituents at C1', C2', C3' and an axially located hydroxyl group at C4'. As a result of this distortion the atoms O1' and C5' as well as C3' and C2' leave the average plane formed by the atoms O1', C2', C3' and C5' in opposite directions by 0.026 Å and 0.024 Å, respectively. The average plane forms dihedral angles (53.3° and 51.9°) with the planes connecting atoms O1', C1', C2' and C3', C4', C5', respectively. The value of torsion angle O1'-C1'-N3-C2 about the glycosyl bond is 84.9°. The puckering parameters [9] of the pyranose ring are q 0.582 Å, θ 3.3° and q_2 0.034 Å.

The obtained values of bond lengths and valent angles summarized in Table 1 and 2 correspond, in general, to their standard values [10]. Molecules 1a within the crystal are associated by way of hydrogen bonding HO4'... O5 = 2.7 Å, the crystal being further stabilized by two more hydrogen bonds involving the water of crystallization and atoms O1' and O2' in the compound; H_2O ...O1' = 2.84 Å, H_2O ...O2' = 2.71 Å.

We have found that the heating of α-D-arabinopyranosylurea, malononitrile and triethyl orthoformate gives 1-(3',4'-O-ethoxymethylene-α-D-arabinopyranosyl)-ureidomethylenemalononitrile (2).

The ethoxymethylene group formed in compound 2 during the condensation is cleaved by heating it in 90% ethanol. This group is stable in basic medium [15,16].

TABLE 1

Bond Distances of Compounds 1a, 5 and 7

with e.s.d.s. in parentheses

Compound	1a	5	7
C1' - C2'	1.536(8)	1.532(9)	1.526(10)
C2' - C3'	1.531(9)	1.543(9)	1.516(11)
C3' - C4'	1.515(9)	1.528(10)	1.526(11)
C4' - C5'	1.505(9)	1.519(10)	1.501(11)
C5' - O1'	1.443(8)	1.422(9)	1.439(9)
C1' - O1'	1.444(7)	1.404(8)	1.419(8)
C2' - O2'	1.429(9)	1.413(8)	1.404(9)
C3' - O3'	1.425(7)	1.430(9)	1.439(9)
C4' - O4'	1.445(9)	1.441(9)	1.445(8)
C1' - N3	1.442(9)	1.480(8)	1.494(8)
C6' - O3'		1.407(9)	
C6' - O4'		1.418(10)	
C6' - O6'		1.369(9)	
C7' - O6'		1.458(10)	
C7' - C8'		1.494(13)	
C2 - N1	1.350(10)	1.346(9)	1.359(9)
C2 - N3	1.538(8)	1.439(8)	1.421(10)
C2 - O2	1.237(8)	1.226(8)	1.249(8)
C4 - N3		1.374(8)	1.381(8)
C4 - C5		1.399(9)	1.408(10)
C4 - N4		1.319(9)	1.305(9)
C5 - C6		1.368(10)	1.393(11)
C5 - C7		1.446(10)	1.463(9)
C6 - N1		1.316(9)	1.311(9)
C7 - N7		1.142(10)	1.138(9)

1-(α-D-Arabinopyranosyl)ureidomethylenemalononitrile (4) precipitates from solution in small white crystals. Three-component condensation also leads to 1-(2',3',4'-tri-O-cetylarabinopyranosyl)ureidomethylenemalononitrile 3.

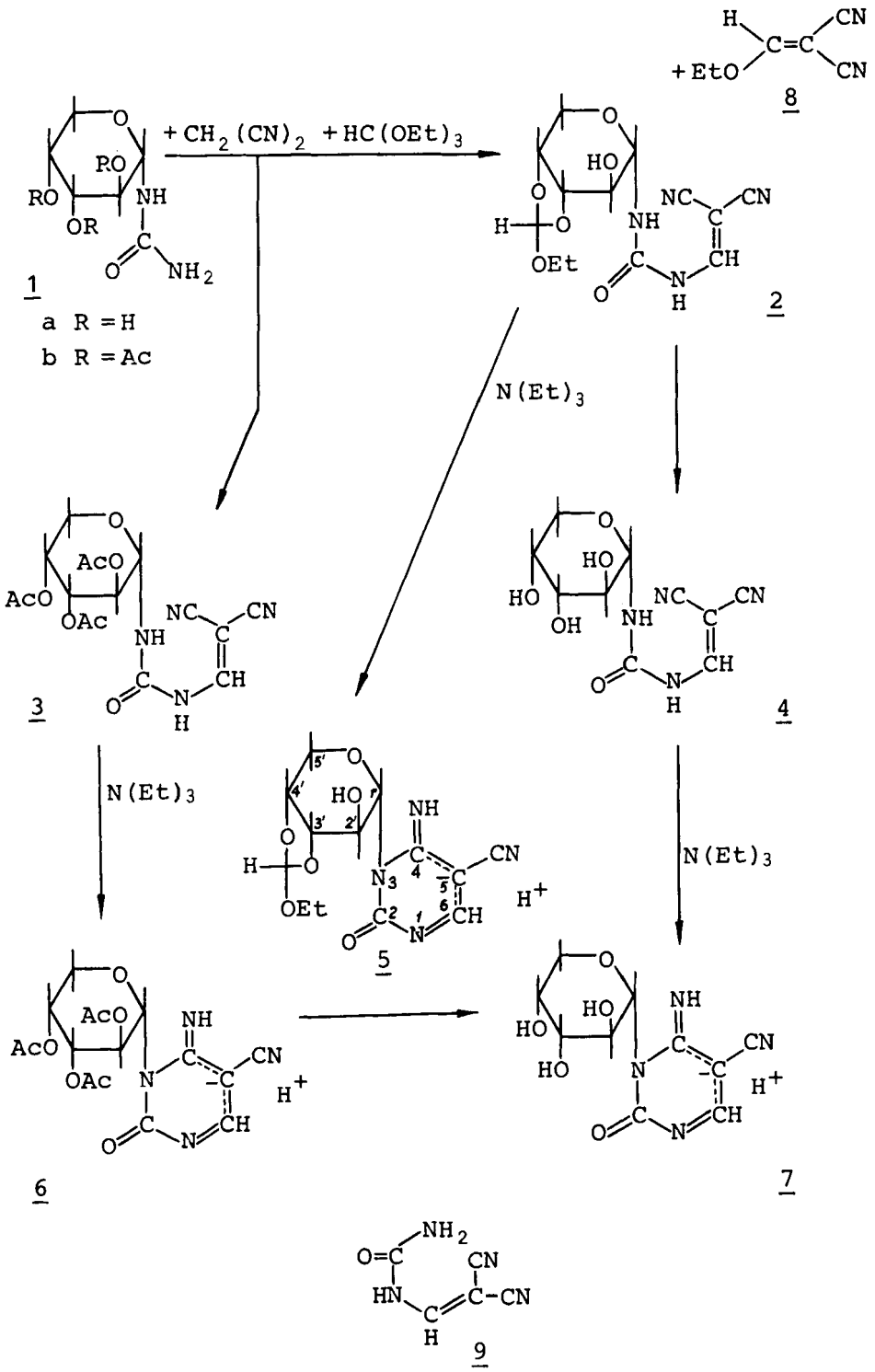
Cyclization of compounds 2-4 to pyrimidine derivatives 5-7 was carried out by heating in 96% ethanol in

TABLE 2

Bond Angles (°) of Compounds 1a, 5 and 7

with e.s.d.s. in parentheses

Compound	1a	5	7
C1' - C2' - C3'	108.1(5)	108.7(5)	109.6(6)
C2' - C3' - C4'	111.4(5)	114.9(6)	109.7(6)
C3' - C4' - C5'	109.5(5)	114.9(6)	108.5(6)
C4' - C5' - O1'	110.2(5)	113.4(6)	108.6(6)
C5' - O1' - C1'	110.5(4)	109.0(5)	113.1(5)
O1' - C1' - C2'	112.0(5)	111.6(5)	117.2(6)
C1' - C2' - O2'	107.4(5)	107.3(5)	108.5(5)
C3' - C2' - O2'	109.4(5)	112.0(5)	113.8(6)
C2' - C3' - O3'	108.8(5)	110.7(6)	107.8(6)
C4' - C3' - O3'	111.2(5)	103.4(6)	112.0(6)
C3' - C4' - O4'	111.9(5)	101.3(5)	111.4(6)
C5' - C4' - O4'	106.8(5)	109.9(6)	107.3(6)
C3' - O3' - C6'		106.5(5)	
C4' - O4' - C6'		108.8(5)	
O3' - C6' - O4'		108.2(6)	
O3' - C6' - O6'		112.1(6)	
O4' - C6' - O6'		113.4(6)	
C6' - O6' - C7'		115.0(6)	
O6' - C7' - C8'		108.2(7)	
O1' - C1' - N3	106.6(5)	108.5(5)	104.1(5)
C2' - C1' - N3	110.2(5)	112.8(5)	110.4(5)
C6 - N1 - C2		118.7(6)	118.8(6)
N1 - C2 - N3	115.2(6)	119.4(6)	120.2(6)
N1 - C2 - O2	122.9(6)	123.2(6)	121.6(7)
N3 - C2 - O2	121.9(6)	117.3(6)	118.2(6)
C2 - N3 - C4		120.9(5)	122.2(6)
C2 - N3 - C1'	120.0(5)	117.2(5)	118.0(5)
C4 - N3 - C1'		121.7(5)	119.6(5)
N3 - C4 - C5		116.5(6)	114.0(6)
N3 - C4 - N4		119.0(6)	122.5(6)
C5 - C4 - N4		124.5(6)	123.5(6)
C4 - C5 - C6		119.7(6)	121.6(6)
C4 - C5 - C7		117.4(6)	119.6(6)
C6 - C5 - C7		122.8(6)	118.8(6)
C5 - C6 - N1		124.4(6)	122.6(7)
C5 - C7 - N7		177.6(8)	177.2(8)



the presence of triethylamine. The structure of compounds 2-4 was assigned by elemental analysis, IR, UV and NMR spectroscopy.

The IR spectra of compounds 2-4 show $\nu_{C=O}$ in the 1740-1755 cm^{-1} range similar to $\nu_{C=O}$ 1750 cm^{-1} of ureidomethylenemalononitrile 9 synthesized by Prystaš and Šorm [14] and $\nu_{C\equiv N}$ at 2231-2250 cm^{-1}. In compound 3, $\nu_{C=O}$ of the acetyl group is also found at 1709 cm^{-1}. It is interesting to note that the UV spectra of compounds 2-4 appear identical in neutral and acidic media (λ_{max} = = 280 nm); however, in 0.1 N NaOH a bathochromic shift of the maximum to 310 nm is observed, indicating ionization of the N3-H bond in the ureidomethylenemalononitrile moiety in compounds 2-4.

Since the results of X-ray analysis failed to reveal any appreciable differences in the geometry of the 6-membered cycle in crystals, the small value $J_{1',2'}$ (5.8-6.0 Hz) in the spectra of compounds 1a and 4 probably does not reflect any deviations in the geometry of the sugar cycle in solution from other compounds investigated by us ($J_{1',2'}$ = 8-9 Hz), but is in fact a virtual constant due to the similar values of chemical shifts found for the protons in the cycle.

The ^1H NMR spectra of compounds 5-7 fail to demonstrate a separate signal from H_5 proton in DMSO solution. It appears likely that this proton under the present conditions is completely dissociated. The ^{13}C NMR spectra

obtained with partial decoupling also lend support to H_5 proton dissociation, since the C_5 signal (76.38 ppm) is a singlet.

Based on the following features the compounds obtained (1a, 4, 7) were assigned to α-isomers:

1. The ^{13}C chemical shifts for α-arabinofuranose are located downfield by ca. 5 ppm, as compared to the ß-isomer. [11]

2. Substitution of the hydroxyl group for an amino or acetamido group brings about an upfield shift of the C1' and C2' resonances by ~20 ppm and ~2 ppm, respectively; the chemical shifts of the remaining carbon atoms being only slightly affected.[11]

3. The ^{13}C chemical shifts calculated for 1a (78 ppm, (C1'); 71 ppm (C2'), 73 ppm (C3'), 70 ppm (C4'), 67 ppm (C5')) appear to be in a better agreement with the experimental findings (Table 3) than the corresponding values calculated for the ß-isomer (73 ppm (C1'), 68 ppm (C2'), 69 ppm (C3'), 70 ppm (C4'), 64 ppm (C5')).

The geometry and conformation of compounds 5 and 7 was studied using X-ray analysis. In these compounds, whose stereoviews are represented in the figures, the dihedral angle formed by the central planes passing across C2', C3', C5', O1' atoms in the pyrimidine moiety amounts to 86.3° and 90.5°, respectively. The pyranose rings, as in compound 1a, are in the distorted chair

TABLE 3

The ^{13}C Chemical Shifts of Compounds 1a, 4 and 7

Compound	C1'	C2'	C3'	C4'	C5'	Remaining C
1a	82.4	71.3	74.4	68.8	66.9	159.4 (CO)
4	81.5	71.1	73.3	67.7	66.1	156.6(CO); 151.9(CH=); 58.8(=C<); 115.6 and 113.7 (C≡N)
7	86.4	67.3	73.8	69.1	69.7	159.4 (C_2) 155.0 (C_4) 165.9 (C_6) 76.4 (C_5) 116.9 (C≡N)

conformation $^1C_4$. Torsion angle values x:O1'-C1'-N3-C4 are -55.8° for 5 and -59.5° for 7.

The packing of molecules within crystals is stabilized in 5 by intermolecular hydrogen bonding of OH...O (O2'...O2 2.922 (7)Å), NH...O (N4...O2 2.757 (7)Å) and NH...H (N4...N1 2.912 (8)Å) types, but in compound 7 only - of OH...N type (O2'...N7 2.903 (8)Å, O3'...N7 3.008 (9)Å, O4'...N1 2.740 (8) Å).

As revealed by X-ray analysis data (Table 1), arabinopyranosylpyrimidines 5-7 occur in an ionized form. This is also indicated by UV spectra, their curves showing a similar pattern in neutral medium and in 0.1 N NaOH solution. At the same time, a hypsochromic shift of both maxima are observed in 0.1 N HCl.

EXPERIMENTAL

The identity of obtained compounds was established by TLC on Silufol-254 plates in system A: propanol - 25% NH_4OH - water, 7:1:2 and system B: chloroform - ethyl acetate, 3:1. The plates were visualized in UV light or with Ehrlich reagent and iodine vapors. Column chromatography was performed with Woelm silicagel. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Model WH-90 (90 MHz) spectrometer with TMS as internal standard. The $[\alpha]_D^{20}$ values were determined on a Perkin-Elmer 141 polarimeter, UV spectra were obtained with a Specord UV-vis spectrometer and IR spectra in vaseline oil were recorded on a UR-20 spectrometer. X-Ray analyses were performed using a Syntex $P2_1$ full-automatic four-circle diffractometer and the XTL structure determination package.

1-(α-D-Arabinopyranosyl)urea 1a was prepared by the following method [6]. The compound with $C_6H_{12}N_2O_5 \cdot H_2O$ composition (m.p. 194-195° (from ethanol+H_2O), lit. m.p. 193° [6]) is crystallized on a monoclinic system with following crystal data: a = 7.784 (1), b = 8.252 (2), c = 7.924 (1) Å, ß = 117.42 (1)°, V = 451.8 Å ^{3}, M = 210.2, d_{calc} = 1.55 g·cm^{-3}, Z = 2, $\mu(CuK_\alpha)$ = 12.4 cm^{-1}, space group $P2_1$.

The intensity data were collected from 0.1 x 0.15 x 0.35 mm crystals by the θ/2θ scanning technique (θ_{max}=

$=75^{\circ}$) using monochromatic Cu radiation. The structure was solved by direct methods using MULTAN program [12] and the nonhydrogen atoms were refined by the full-matrix least squares method (633 reflections with $I \geqslant 2\sigma_I$) in the anisotropic approximation including the positions of hydrogen atoms identified from a difference map of electron density distribution up to $R = 0.044$. The coordinates of nonhydrogen atoms with their e.s.d.'s. in parentheses are listed in Table 4.

The ^1H NMR spectrum of 1a, DMSO-d_6, δ: 6.52(1H,d, J = 9.4 Hz, NH); 5.67(2H,s,NH_2); 4.49(1H,dd,J = 9.4 and 5.8 Hz, $H_{1'}$); 4.78(2H,d,J = 4 Hz,OH); 4.46(1H,d,J = 4 Hz, OH); 3.7-3.2 ppm (5H,m,$H_{2'}$,$H_{3'}$,$H_{4'}$,$H_{5'}$).

1-(2',3',4'-Tri-O-acetyl-D-arabinopyranosyl)urea 1b (m.p. 211-213° (from ethanol+H_2O), lit. m.p. 212-213° [2]) was prepared by the method [2]. ^1H NMR, DMSO-d_6, δ: 6.65 (1H,d,J = 9.6 Hz,NH); 5.76 (2H,s,NH_2); 5.2-4.9 (4H, m,$H_{1'}$,$H_{2'}$,$H_{3'}$,$H_{4'}$); 3.77 (2H,s,$H_{5'}$); 2.05, 1.96 and 1.92 ppm (3H,3H,3H,s,$COCH_3$).

1-(3',4'-O-Ethoxymethylene-α-D-arabinopyranosyl)-ureidomethylenemalononitrile 2. The suspension of arabinopyranosylurea 1a (9.6 g, 0.05 M) and malononitrile (3.3 g, 0.05 M) in 54 ml of triethyl orthoformate was heated for 15 h on a magnetic stirrer at 80°C. After standing for 10 h at 5°C, 6.0 g (37%) of the substance 2 precipitated and was obtained by filtration, m.p. 187-189°C (decomp., from ethanol+ether). As revealed by TLC

in system A, the filtrate contains compounds 2 (R_f = = 0.75), 4 (R_f = 0.47) and arabinopyranosylurea 1a (R_f = = 0.16), as well as ethoxymethylenemalononitrile 8 [13] (system B; R_f = 0.5). Found: C 48.1; H 5.0; N 16.8%. $C_{13}H_{16}N_4O_6$ calculated: C 48.1; H 5.0; N 17.3%. $[\alpha]_D^{20}$ - 38.8° (c = 0.5 DMS). IR cm^{-1}, 3450, 3269, 2245, 1755, 1620, 1561. UV λ_{max} nm ($\varepsilon \cdot 10^4$) EtOH: 280 (1.5); 0.1 N HCl: 280 (1.5); 0.1 N NaOH: 310 (1.3). ^1H NMR, DMSO-d_6, δ: 10.67 (1H,d,J = 8.0 Hz,N^3H); 8.23 (1H,d,J = 8 Hz, CH=); 7.67 (1H,d,J = 8.8 Hz,N^1H); 5.83 (1H,s,$HC(-O-)_3$); 5.49 (1H,d,J = 4 Hz,OH); 4.63 (1H,t,J = 8.5 Hz,$H_{1'}$); 4.2 (2H,m, $H_{3'}$,$H_{4'}$); 3.96 and 3.78 (2H, AB - q, J = 13.6 Hz,$H_{5'}$); 3.53 (2H,q,J = 6.4 Hz,OCH_2); 3.23 (1H,m,$H_{2'}$); 1.15 ppm (3H,t,J = 6.4 Hz,CH_3).

1-(2',3',4'-Tri-O-acetyl-α-D-arabinopyranosyl)ureidomethylenemalononitrile 3. The mixture of 1-(2',3',4'-tri-O-acetyl-α-D-arabinopyranosyl)urea 1b (3.18 g, 0.01 M), malononitrile (0.8 g, 0.012 M) and 15 ml of triethyl orthoformate was heated on a magnetic stirrer for 8 h at 78-80°C and then for 10 h at 60°. The unreacted compound 1b (1.9 g) was filtered off. The filtrate containing acetylated noncyclic product 3 and ethoxymethylenemalononitrile 8 was evaporated to 5 ml and the mixture was separated on a silica gel column. Fraction R_f = 0.68 (System A) was collected following chloroform elution and evaporated to dryness. Yield: 1.12 g (28%); m.p. 200-203° (from ethanol). Found: C 48.9; H 4.3; N 14.2%.

$C_{16}H_{18}N_4O_8$ calculated: C 48.7; H 4.6; N 14.2%. $[\alpha]_D^{20}$ - 6.2° (c = 0.5 DMF). IR cm^{-1}: 3372, 3200, 2245, 2233, 1740, 1709, 1626. UV λ_{max} nm ($\varepsilon \cdot 10^4$) EtOH: 277 infl., 311 (1.5); 0.1 N HCl: 277 (1.4); 0.1 N NaOH: 277 infl., 311 (1.3). ^1H NMR, DMSO-d_6, δ: 10.59 (1H,d,J = 8 Hz,N^3H); 8.34 (1H,d,J = 8 Hz, CH=); 7.92 (1H,d,J = 8.4 Hz, N^1H); 5.2-4.9 (4H,m,H_1',H_2',H_3',H_4'); 3.92 and 3.78 (2H, AB - kv, J = 13 Hz,H_5'); 2.07, 1.99, 1.92 ppm (3H,3H,3H,s, $COCH_3$).

1-(α-D-Arabinopyranosyl)ureidomethylenemalononitrile 4. The solution of compound 2 (5.1 g, 0.016 M) in 30 ml 90% ethanol was boiled for 3 h to give a white precipitate consisting of small crystals of compound 4 (R_f = 47). As found chromatographically, the reaction mixture also contains compounds 7 (R_f = 0.37) and 9 (R_f = = 0.79) as well as the starting agent 2 (R_f = 0.75) in system A. Yield: 35%, m.p. 175-180° (decomp., after recrystallization from ethanol). Found: C 41.7; H 4.8; N 19.3%. $C_{10}H_{12}N_4O_5 \cdot H_2O$ calcd.: C 41.9; H 4.9; N 19.6%. $[\alpha]_D^{20}$ -31.1° (c = 1.0 H_2O). IR cm^{-1}: 3380-3200, 2231, 1750, 1680, 1650 shoulder, 1631, 1555. UV, λ_{max} nm ($\varepsilon \cdot 10^4$) H_2O: 280 (1.3); 0.1 N HCl: 280 (1.3); 0.1 N NaOH: 310 (1.2). ^1H NMR, DMSO-d_6, δ: 10.87 (1H,d,J = 8 Hz, N^3H); 8.32 (1H,d,J = 8 Hz, CH=); 7.87 (1H,d,J = 8.8 Hz, N^1H); 5.10, 4.85, 4.46 (1H,1H,1H,d,J = 4 Hz,OH); 4.67 (1H,dd,J = 8.8 and 5.9 Hz,H_1'); 3.2-3.7 (5H,m,H_2',H_3', H_4',H_5').

2-Oxo-4-imino-5-cyano-3-(3',4'-O-ethoxymethylene-α-D-arabinopyranosyl)-2,3,4,5-tetrahydropyrimidine 5. Compound 2 (3.3 g, 0.01 M) was boiled for 3.5-4 h in 20 ml of 96% ethanol with 0.1 ml of triethylamine until the spot of the cyclic compound 5 (R_f = 0.59) appeared instead of that of compound 2 (R_f = 0.75), as evidenced by TLC in system A. Following evaporation to 5 ml and standing for 24 h at 5°C, cream-coloured crystals of compound 5 were formed. Yield: 50%, m.p. 189-191° (from ethanol + H_2O). Found: C 48.2; H 4.8; N 17.0%. $C_{13}H_{16}N_4O_6$ calcd.: C 48.1; H 5.0; N 17.3%. $[\alpha]_D^{20}$ -125.4° (c = 0.5 DMF). IR cm^{-1}: 3385, 2232, 1675, 1619, 1558. UV λ_{max} nm ($\varepsilon \cdot 10^4$) H_2O: 248 (1.8), 307 (1.4); 0.1 N HCl: 230 (1.6), 291 (1.2); 0.1 N NaOH: 245 (1.2), 319 (1.5). ^1H NMR, DMSO-d_6, δ: 8.21 (1H,s,H_6); 8.0 (2H,broad sh,NH and H_5); 5.89 (1H,s,H(-O-)$_3$); 5.76 (1H,d,J = 4 Hz,OH); 5.74 (1H, d,J = 9.2 Hz,$H_{1'}$); 4.3-3.9 (5H,m,$H_{2'}$,$H_{3'}$,$H_{4'}$,$H_{5'}$); 3.52 (2H,q,J = 6.8 Hz, OCH_2); 1.11 ppm (3H,t,J = 6.8 Hz,CH_2).

Compound 5 - $C_{13}H_{15}O_6N_4$ was crystallized on a orthorhombic system with the following crystal data obtained: a = 6.767 (1), b = 12.545 (1), c = 17.619 (2) Å, V = = 1495.7 $Å^3$, M = 323.32, $d_{calc.}$ = 1.44 $g \cdot cm^{-3}$, Z = 4, $\mu(CuK_\alpha)$ = 10.0 cm^{-1}, space group $P2_12_12_1$. Intensity data were collected from 0.1 x 0.15 x 0.4 mm crystals. The method of structure determination is similar to that of structure 1a. The final reliability factor value is

0.060. The nonhydrogen atomic coordinates are presented in Table 4.

2-Oxo-4-imino-5-cyano-3-(α-D-arabinopyranosyl)-2,3,4,5-tetrahydropyrimidine 7 was prepared similarly to compound 5 by boiling the ureidomethylenemalononitrile derivative 4 (1.8 g, 0.007 M) in 40 ml of 90% ethanol with 0.1 ml of triethylamine. After boiling during 0.5 h a white substance 7 began to precipitate from the reaction mixture. Yield: 72%, m.p. 216-219° (decomp., from ethanol + H_2O). Found: C 44.7; H 4.5; N 20.7%. $C_{10}H_{12}N_4O_5$ calcd.: C 44.8; H 4.5; N 20.8%. $[\alpha]_D^{20}$ - 111.4° (c = 0.5 DMF). R_f = 0.37 (system A). IR cm^{-1}: 3415, 3330, 2245, 1700 sh., 1665, 1605, 1558. UV, λ_{max} nm ($\varepsilon \cdot 10^4$) H_2O: 248 (1.3); 319 (1.4). ^1H NMR DMSO-d_6, δ: 8.7 (1H,broad s,H_5); 8.23 (1H,s,H_6); 7.7 (1H,broad s, NH); 5.88 (1H,d,J = 8.8 Hz, $H_{1'}$); 5.33 and 5.09 (1H and 1H,d,J = 4 Hz,OH); 5.4 (1H,broad s,OH); 4.03 (1H,m,$H_{2'}$); 3.5-3.7 ppm (4H,m,$H_{3'}$,$H_{4'}$,$H_{5'}$).

Crystal data: a = 7.063 (1), b = 8.810 (1), c = = 18.059 (2) Å, V = 1123.8 $Å^3$, M = 268.2, $d_{calc.}$ = 1.59 $g \cdot cm^{-3}$, Z = 4, $\mu(CuK_\alpha)$ = 11.2 cm^{-1}, orthorhombic space group $P2_12_12_1$. Intensity data were collected from a 0.13 x 0.2 x 0.3 mm crystal. The method of structure determination is similar to that of structure 1a. The final R value is 0.057. The nonhydrogen atomic coordinates are listed in Table 4.

TABLE 4

Atomic Coordinates ($\times 10^4$) of Nonhydrogen Atoms in Compounds 1a, 5 and 7

Compound	1a			5			7		
Atom	x/a(σ)	y/b(σ)	z/c(σ)	x/a(σ)	y/b(σ)	z/c(σ)	x/a(σ)	y/b(σ)	z/c(σ)
O1'	-5531(5)	-4162(0)	-1218(5)	4534(7)	2055(4)	2141(2)	1715(6)	4332(6)	3799(3)
O2'	-3947(5)	-6930(7)	-3870(6)	2953(8)	2943(4)	279(2)	-3427(7)	4573(7)	3498(3)
O3'	-8093(5)	-7395(8)	-5723(6)	6402(7)	4446(4)	835(8)	-2760(8)	1315(7)	3395(3)
O4'	-9104(5)	-4423(8)	-4482(6)	7596(7)	3787(4)	1956(3)	756(9)	1514(6)	4273(2)
O6'				9523(7)	4933(4)	1224(3)			
O2	-901(5)	-4593(8)	1642(6)	-480(7)	1651(4)	1239(3)	-618(9)	7954(6)	3451(3)
N1	83(7)	-2650(9)	244(8)	69(8)	-44(4)	853(3)	-604(9)	8709(7)	4656(3)
N3	-2707(6)	-4064(8)	-1504(6)	2736(7)	1111(4)	1225(3)	-311(8)	6072(6)	4319(3)
N4				6000(8)	548(5)	1186(4)	302(9)	4216(6)	5226(3)
N7				6029(10)	-2009(5)	367(4)	-659(11)	6076(8)	6963(3)
C1'	-4243(7)	-5127(9)	-1658(8)	3307(10)	2181(5)	1504(4)	-134(10)	4935(8)	3709(3)
C2'	-5279(7)	-5856(10)	-3664(8)	4294(10)	2864(5)	891(4)	-1783(10)	3817(9)	3731(3)
C3'	-7028(7)	-6820(9)	-3823(8)	4790(11)	3964(5)	1233(4)	-1303(10)	2428(9)	3273(4)
C4'	-8291(6)	-5803(10)	-3244(8)	5501(11)	3940(6)	2056(4)	651(12)	1837(9)	3490(4)
C5'	-7089(7)	-5145(10)	-1272(8)	4653(13)	3043(4)	2534(4)	2085(10)	3050(9)	3327(4)
C6'				8134(12)	4139(6)	1220(5)			
C7'				8923(12)	5909(6)	1610(5)			
C8'				10731(16)	6561(7)	1756(6)			
C2	-1154(7)	-3809(9)	215(8)	664(10)	918(6)	1101(4)	-517(11)	7625(9)	4122(4)
C4				4123(10)	358(5)	1035(4)	-125(9)	5609(9)	5046(3)
C5				3409(10)	-590(5)	718(4)	-407(10)	6774(9)	5567(3)
C6				1416(10)	-748(5)	656(4)	-584(10)	8287(9)	5352(4)
C7				4844(12)	-1398(6)	521(4)	-514(11)	6402(9)	6356(4)
O(H20)	-6597(6)	-1120(8)	-3092(6)						

2-Oxo-4-imino-5-cyano-(2',3',4'-tri-O-cetyl-α-D-arabinopyranosyl)-1,2,3,4-tetrahydropyrimidine 6 was similarly obtained. Yield: 63%, m.p. 210-212° (decomp., from ethanol). Found: C 48.3; H 4.8; N 14.1%. $C_{16}H_{18}N_4O_8$ calcd.: C 48.7; H 4.6; N 14.2%. $[\alpha]_D^{20}$ -111.8° (c = 0.5 DMF). R_f = 0.69 (system A). IR cm^{-1}: 3380, 2238, 1755, 1690, 1635, 1600, 1555. UV, λ_{max} nm ($\varepsilon \cdot 10^4$) EtOH: 248 (1.3); 313 (1.0); 0.1 N HCl: 230 (1.1), 300 (0.9); 0.1 N NaOH: 2.46 (1.2); 319 (1.4). ^1H NMR, DMSO-d_6, δ: 8.25 (1H,s,H_6); 8.0 (2H,broad s,NH and H_5); 6.43 (1H,d,J = 8.4 Hz,$H_{1'}$); 5.63 (1H,dd,J = 8.4 and 9.0 Hz,$H_{2'}$); 5.3 (2H,m,$H_{3'}$ and $H_{4'}$); 4.16 and 4.02 (2H, AB-q,J = 14.0 Hz, $H_{5'}$); 2.04, 1.94, 1.86 ppm (3H,3H,3H,s,$COCH_3$).

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