

C(4)	0.4328 (4)	-0.2142 (12)	0.3055 (3)	0.061 (3)
C(5)	0.5205 (4)	-0.1269 (14)	0.3222 (4)	0.073 (3)
C(6)	0.5564 (4)	0.0774 (14)	0.3734 (4)	0.071 (3)
C(7)	0.5052 (4)	0.2034 (12)	0.4102 (3)	0.063 (3)
C(8)	0.4180 (3)	0.1131 (10)	0.3933 (3)	0.044 (2)
C(9)	0.3459 (3)	0.2085 (12)	0.4211 (3)	0.050 (2)
O(1)	0.1894 (2)	0.0764 (7)	0.3909 (2)	0.056 (2)
O(2)	0.2319 (3)	-0.2992 (9)	0.2979 (2)	0.072 (2)
O(9)	0.3478 (2)	0.3869 (8)	0.4649 (2)	0.074 (2)
C(10)	0.1809 (3)	-0.1178 (12)	0.4447 (3)	0.063 (3)
C(11)	0.0834 (3)	-0.1074 (12)	0.4384 (3)	0.062 (3)
C(12)	0.0192 (3)	-0.2037 (11)	0.3623 (3)	0.058 (3)
N(13)	-0.0749 (3)	-0.1952 (9)	0.3582 (2)	0.053 (2)
C(14)	-0.1203 (3)	-0.4119 (13)	0.3597 (3)	0.049 (3)
C(15)	-0.2153 (4)	-0.3647 (12)	0.3594 (4)	0.059 (3)
O(14)	-0.0931 (3)	-0.6402 (8)	0.3644 (3)	0.090 (2)
F(1)	-0.2755 (2)	-0.5044 (8)	0.3055 (2)	0.108 (2)
F(2)	-0.2421 (2)	-0.1163 (7)	0.3503 (2)	0.095 (2)
F(3)	-0.2227 (2)	-0.4471 (9)	0.4225 (2)	0.113 (2)

Table 2. Geometric parameters (Å, °)

N(1)—C(2)	1.389 (8)	N(1)—C(9)	1.382 (6)
N(1)—O(1)	1.377 (6)	C(2)—C(3)	1.490 (8)
C(2)—O(2)	1.192 (6)	C(3)—C(4)	1.369 (9)
C(3)—C(8)	1.375 (7)	C(4)—C(5)	1.375 (9)
C(5)—C(6)	1.377 (9)	C(6)—C(7)	1.393 (10)
C(7)—C(8)	1.373 (7)	C(8)—C(9)	1.495 (9)
C(9)—O(9)	1.208 (7)	O(1)—C(10)	1.445 (7)
C(2)—N(1)—C(9)	115.1 (5)	C(2)—N(1)—O(1)	122.2 (4)
C(9)—N(1)—O(1)	122.4 (5)	N(1)—C(2)—C(3)	103.4 (4)
N(1)—C(2)—O(2)	124.6 (6)	C(3)—C(2)—O(2)	132.0 (6)
C(2)—C(3)—C(4)	129.0 (5)	C(2)—C(3)—C(8)	109.2 (5)
C(4)—C(3)—C(8)	121.7 (5)	C(3)—C(4)—C(5)	117.4 (5)
C(4)—C(5)—C(6)	121.4 (7)	C(5)—C(6)—C(7)	121.2 (6)
C(6)—C(7)—C(8)	116.8 (5)	C(3)—C(8)—C(7)	121.5 (5)
C(3)—C(8)—C(9)	108.5 (4)	C(7)—C(8)—C(9)	130.0 (5)
N(1)—C(9)—C(8)	103.8 (5)	N(1)—C(9)—O(9)	126.3 (6)
C(8)—C(9)—O(9)	129.9 (5)	N(1)—O(1)—C(10)	108.7 (3)

Data collection and reduction: *P3/PC Data Collection* (Siemens, 1989). Program package used to solve and refine the structure: *SHELXTL/PC* (Siemens, 1990). Refinement was by full-matrix least-squares methods.

We thank Dr Paul Kong Thoo Lin (MRC Cambridge) for providing the crystals and the Research Foundation of Leuven for financial support. LVM is a Research Associate of the National Fund for Scientific Research (Belgium).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55684 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1028]

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*Acta Cryst.* (1993). **C49**, 626–628

## An Original Linkage Between Arabinose and a Pyranopyrimidine Derivative via a Sulfur Atom

ALAIN TOMAS

*Laboratoire de Physique (URA 200), Faculté des Sciences Pharmaceutiques et Biologiques de Paris V, 4 avenue de l'Observatoire, 75270 Paris CEDEX 06, France*

NGUYEN HUY DUNG

*Laboratoire de Chimie Minérale 2, Faculté de Pharmacie, 1 rue Jean-Baptiste Clément, 92296 Châtenay Malabry CEDEX, France*

BERNARD VIOSSAT

*Laboratoire de Chimie Générale, UFR de Médecine et Pharmacie, 34 rue du Jardin des Plantes, 86034 Poitiers CEDEX, France*

ANDRÉ ESANU AND ALAIN ROLLAND†

*Institut Henri Beaufour, 17 avenue Henri Descartes, 92350 Le Plessis Robinson, France*

(Received 13 April 1992; accepted 5 October 1992)

## Abstract

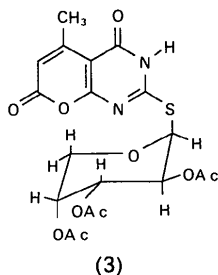
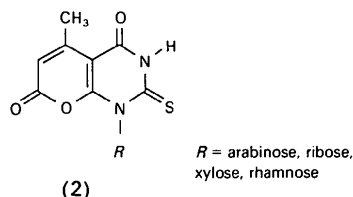
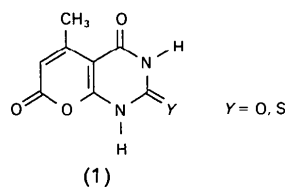
The structure of 5-methyl-2-[(2,3,4-tri-*O*-acetyl- $\beta$ -D-arabinopyranosyl)thio]-3,4-dihydro-7*H*-pyrano[2,3-*d*]pyrimidine-4,7-dione, C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>10</sub>S, is described. This compound consists of a sugar ring and a planar base (pyranopyrimidine derivative) linked unusually by an S atom. The sugar ring is in a <sup>4</sup>C<sub>1</sub> chair conformation and makes dihedral angles of 74.5 (4) and 75.7 (4)° with the pyran and pyrimidine rings. The S atom occupies an axial position on the sugar ring and lies 2.461 (9) Å out of the corresponding mean plane.

## Comment

Synthetic nucleosides are widely studied and used therapeutically as antiviral (Lin *et al.*, 1991), anti-tumor (Ramasamy *et al.*, 1990) and antibiotic compounds (Knapp & Shieh, 1991). Our aim is to synthesize nucleosides by substituting the heterocyclic base (pyrimidine or purine) by a pyranopyrimidine ring (1). From this compound, the nucleosides (2) were synthesized and their antiviral

† This publication is dedicated to Marie-Eve Rolland.

activity was studied (Esanu, 1984). During this work, the thioglycoside (3) was isolated and the structure was determined by X-ray diffraction on a single crystal.

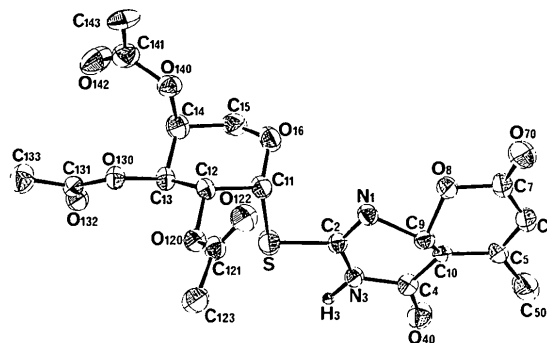


*Dihydro-7H-pyrano[2,3-d]pyrimidine-4,7-dione moiety (TPPM)*. The deviations of each atom of the heterocyclic rings *P1* [N(1)—C(2)—N(3)—C(4)—C(10)—C(9)] and *P2* [C(5)—C(6)—C(7)—O(8)—C(9)—C(10)] from the mean plane are within 0.013 (9) Å. The S and O(40) atoms deviate from *P1* by 0.040 (1) and  $-0.01$  (2) Å; the C(50) and O(70) atoms deviate from *P2* by  $-0.05$  (2) Å and  $-0.03$  (1) Å, respectively. The dihedral angle between *P1* and *P2* is  $2.8$  (4)°.

*2,3,4-Tri-O-acetylarabinopyranosyl ring (ARA)*. The acetylarabinose ring adopts a  ${}^4C_1$  chair conformation (which corresponds to  ${}^{14}C_{11}$  in our numbering) where the S and O(140) atoms are axially oriented, O(120) and O(130) occupying an equatorial position, in contrast to the  $1C(D)$  conformation adopted in 1,2,3,4-tetra-*O*-acetyl- $\beta$ -D-arabinopyranose (James & Stevens, 1974). The average atom deviation from the best mean plane *P3* involving the C(12), C(13), C(15), O(16) atoms is 0.017 (6) Å. The C(11) and C(14) atoms are displaced from *P3* by 0.67 (2) and  $-0.64$  (2) Å. The C(11)—O(16) bond is significantly shorter than the corresponding length [1.4316 (6) Å] reported by Longchambon *et al.* (1985) in  $\beta$ -DL-arabinose but it is in good agreement with that in tri-*O*-acetyl- $\beta$ -D-

arabinopyranosyl bromide (Corfield, Mohren, Durette & Horton, 1972). The shortening of the C(11)—O(16) length is induced by the polarizability of the C(11)-bonded S atom. This suggests a partial double-bond character for the C(11)—O(16) bond.

*Thioarabinosidic linkage*. The S atom bridges the ARA and TPPM rings. It lies nearly in the *P1* and *P2* mean planes and assumes an axial position on the acetylarabinose ring. The dihedral angles between the mean plane *P3* and the *P1* and *P2* planes are  $74.5$  (4) and  $75.7$  (4)°, respectively. The orientation of the TPPM moiety relative to the ARA ring may be described by the torsion angles N(3)—C(2)—S—C(11) =  $-172.9$  (7), N(1)—C(2)—S—C(11) =  $8.7$  (9), C(2)—S—C(11)—O(16) =  $73.7$  (8) and C(2)—S—C(11)—C(12) =  $-164.1$  (7)°. An intramolecular hydrogen bond N(3)—H(3)⋯O(132') is observed [2.88 (1) Å;  $169$  (1)°; symmetry code (i)  $-\frac{1}{2} + x, \frac{1}{2} - y, -z$ ].



## Refinement

Final  $R = 0.044$  $wR = 0.047$  $S = 2.0$ 

991 reflections

289 parameters

 $w = 1/\sigma^2(F)$  $(\Delta/\sigma)_{\max} = 0.89$  $\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$ Atomic scattering factors  
from *International Tables*  
for X-ray Crystallography  
(1974, Vol. IV)

C(10)—C(5)—C(50)	121 (1)	C(11)—O(16)—C(15)	114.9 (9)
C(5)—C(6)—C(7)	124 (1)	C(121)—O(120)—C(12)	114.6 (8)
O(70)—C(7)—C(6)	130 (1)	O(122)—C(121)—O(120)	123 (1)
O(70)—C(7)—O(8)	115 (1)	O(122)—C(121)—C(123)	126 (1)
C(6)—C(7)—O(8)	116 (1)	O(120)—C(121)—C(123)	111 (1)
C(9)—O(8)—C(7)	121.9 (9)	C(131)—O(130)—C(13)	116.0 (9)
O(8)—C(9)—N(1)	110.6 (9)	O(132)—C(131)—O(130)	123 (1)
O(8)—C(9)—C(10)	123 (1)	O(132)—C(131)—C(133)	125 (1)
N(1)—C(9)—C(10)	127 (1)	O(130)—C(131)—C(133)	112 (1)
C(9)—C(10)—C(5)	118 (1)	C(141)—O(140)—C(14)	121 (1)
C(9)—C(10)—C(4)	117 (1)	O(142)—C(141)—O(140)	118 (1)
C(5)—C(10)—C(4)	125 (1)	O(142)—C(141)—C(143)	130 (1)
O(16)—C(11)—C(12)	108.8 (9)	O(140)—C(141)—C(143)	111 (1)
O(16)—C(11)—S	113.7 (7)	O(2)—S—C(11)	99.7 (5)
C(12)—C(11)—S	109.3 (7)	C(2)—N(1)—C(9)	114.7 (9)
O(120)—C(12)—C(13)	107.3 (9)	N(1)—C(2)—S	122.2 (8)
O(120)—C(12)—C(11)	110.4 (9)	N(3)—C(2)—S	113.3 (8)
C(13)—C(12)—C(11)	110.4 (9)	N(1)—C(2)—N(3)	124.5 (9)
O(130)—C(13)—C(12)	107 (1)		

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

S	x	y	z	$U_{eq}$
S	0.4338 (4)	0.5072 (3)	0.0445 (1)	0.065 (2)
N(1)	0.444 (1)	0.6952 (8)	0.1241 (4)	0.049 (6)
C(2)	0.382 (1)	0.591 (1)	0.1087 (4)	0.043 (7)
N(3)	0.2692 (9)	0.5381 (7)	0.1394 (4)	0.043 (5)
C(4)	0.208 (1)	0.590 (1)	0.1912 (5)	0.048 (7)
C(5)	0.236 (1)	0.776 (1)	0.2620 (5)	0.058 (8)
C(6)	0.314 (2)	0.883 (1)	0.2748 (5)	0.071 (9)
C(7)	0.432 (2)	0.925 (1)	0.2400 (5)	0.059 (8)
O(8)	0.4650 (8)	0.8531 (7)	0.1883 (3)	0.055 (5)
C(9)	0.390 (1)	0.749 (1)	0.1744 (5)	0.045 (7)
C(10)	0.274 (1)	0.707 (1)	0.2090 (5)	0.044 (6)
C(11)	0.598 (1)	0.595 (1)	0.0232 (5)	0.055 (7)
C(12)	0.640 (1)	0.562 (1)	-0.0427 (5)	0.047 (7)
C(13)	0.683 (1)	0.428 (1)	-0.0471 (5)	0.053 (8)
C(14)	0.807 (1)	0.405 (1)	-0.0030 (5)	0.064 (8)
C(15)	0.767 (1)	0.447 (1)	0.0605 (5)	0.069 (9)
O(16)	0.715 (1)	0.5730 (8)	0.0605 (3)	0.066 (6)
O(40)	0.1079 (9)	0.5360 (7)	0.2155 (4)	0.073 (6)
C(50)	0.116 (1)	0.733 (1)	0.3026 (6)	0.09 (1)
O(70)	0.508 (1)	1.0119 (8)	0.2475 (4)	0.089 (7)
O(120)	0.5183 (8)	0.5804 (6)	-0.0829 (3)	0.052 (5)
C(121)	0.497 (1)	0.702 (1)	-0.1007 (5)	0.061 (8)
O(122)	0.562 (1)	0.7873 (8)	-0.0797 (4)	0.080 (6)
C(123)	0.381 (1)	0.709 (1)	-0.1483 (6)	0.082 (9)
O(130)	0.7287 (8)	0.4073 (7)	-0.1084 (3)	0.052 (5)
C(131)	0.727 (1)	0.287 (1)	-0.1275 (5)	0.054 (8)
O(132)	0.6786 (9)	0.2040 (7)	-0.0976 (4)	0.060 (5)
C(133)	0.792 (1)	0.273 (1)	-0.1896 (6)	0.08 (1)
O(140)	0.9319 (9)	0.4742 (7)	-0.0243 (3)	0.062 (5)
C(141)	1.043 (2)	0.416 (1)	-0.0529 (7)	0.08 (1)
O(142)	1.040 (1)	0.3035 (9)	-0.0565 (5)	0.103 (8)
C(143)	1.152 (1)	0.506 (1)	-0.0746 (6)	0.085 (9)

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S—C(2)	1.75 (1)	C(11)—C(12)	1.55 (1)
S—C(11)	1.84 (1)	C(12)—O(120)	1.45 (1)
N(1)—C(2)	1.30 (1)	C(12)—C(13)	1.49 (1)
N(1)—C(9)	1.35 (1)	C(13)—O(130)	1.44 (1)
N(3)—C(2)	1.36 (1)	C(13)—C(14)	1.52 (2)
N(3)—C(4)	1.39 (1)	C(14)—O(140)	1.45 (1)
C(4)—O(40)	1.21 (1)	C(14)—C(15)	1.52 (2)
C(4)—C(10)	1.45 (1)	C(15)—O(16)	1.43 (1)
C(5)—C(6)	1.39 (2)	O(120)—C(121)	1.37 (1)
C(5)—C(10)	1.43 (1)	C(121)—O(122)	1.19 (1)
C(5)—C(50)	1.49 (2)	C(121)—C(123)	1.50 (2)
C(6)—C(7)	1.41 (2)	O(130)—C(131)	1.36 (1)
C(7)—O(8)	1.41 (1)	C(131)—O(132)	1.19 (1)
C(7)—O(70)	1.17 (1)	C(131)—C(133)	1.51 (2)
O(8)—C(9)	1.35 (1)	O(140)—C(141)	1.35 (1)
C(9)—C(10)	1.39 (1)	C(141)—O(142)	1.21 (1)
C(11)—O(16)	1.38 (1)	C(141)—C(143)	1.47 (2)
C(2)—N(3)—C(4)	123.4 (9)	O(130)—C(13)—C(14)	111.2 (9)
O(40)—C(4)—N(3)	119 (1)	C(12)—C(13)—C(14)	108 (1)
O(40)—C(4)—C(10)	128 (1)	O(140)—C(14)—C(13)	107.6 (9)
N(3)—C(4)—C(10)	114 (1)	O(140)—C(14)—C(15)	110 (1)
C(6)—C(5)—C(10)	118 (1)	C(13)—C(14)—C(15)	111 (1)
C(6)—C(5)—C(50)	121 (1)	O(16)—C(15)—C(14)	111 (1)

Data collection: All intensities were corrected for Lorentz and polarization effects. The structure was determined by direct methods using the program *MULTAN88* (Debaerdemaeker *et al.*, 1988). Full-matrix least-squares refinement on  $F$  magnitudes with anisotropic thermal parameters for non-H atoms and isotropic parameters for H atoms was performed with *ORXFLS* (Busing, 1971). The best mean planes were calculated using *BP7C* (Ito & Sugarawa, 1983). Illustrations were generated with the program *ORTEPII* (Johnson, 1976). Atomic coordinates are listed in Table 1 and bond lengths in Table 2. The molecular conformation is given in Fig. 1.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55622 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1010]

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