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# A Triacetyl Derivation of a Pyrano[3,2-g]-pteridine

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## Abstract

The structure and stereochemistry of the title compound, (3R,4R,4aS,10aR)-5-acetyl-3,4,4a,5,6,7,10,10a-octahydro-8-methoxy-7-methyl-6-oxo-2H-pyrano[3,2-g]pteridin-3,4-diyl diacetate, $C_{17}H_{22}N_4O_8$, is established, with *cis* H

atoms at the A/B ring fusion. Molecules are linked by N—H···O hydrogen bonds [N···O 2.816(5) Å] to form infinite spirals about $2_1$ screw axes.

## Comment

The pteridine ring system has been the subject of many synthetic efforts because of its ubiquitous occurrence in nature (Pfleiderer, 1992). Among the most interesting naturally occurring pteridine systems are the 6-polyhydroxyalkyl derivatives such as biopterine and neopterine. The initial synthesis of this class of compounds was achieved by the reaction between a carbohydrate derivative and a conveniently substituted 5,6-diaminopyrimidine (Viscontini, Provenzale, Ohlgart & Mallevialle, 1970; Schircks, Bieri & Viscontini, 1985); a drawback was that these reactions usually yielded a complex mixture of many reaction products. Soyka, Pfleiderer & Prewo (1990) investigated this reaction type in more detail and found that under a nitrogen atmosphere at 333 K in acidic media, condensation between the diaminopyrimidine and the phenylhydrazone of the corresponding aldose led cleanly to pyrano[2,3-g]pteridine derivatives.

Using the conditions described by Soyka, Pfleiderer & Prewo (1990), we reacted 5,6-diamino-2-methoxy-3-methylpyrimidin-4(3H)-one, (I), with D-xylose phenylhydrazone, (II). The pteridine (III) so obtained was converted to its crystalline triacetyl derivative; this yielded crystals suitable for X-ray study, which identified the derivative as the title compound (IV), shown in Fig. 1 with the numbering scheme.



(I) + (II)



(III)



(IV)
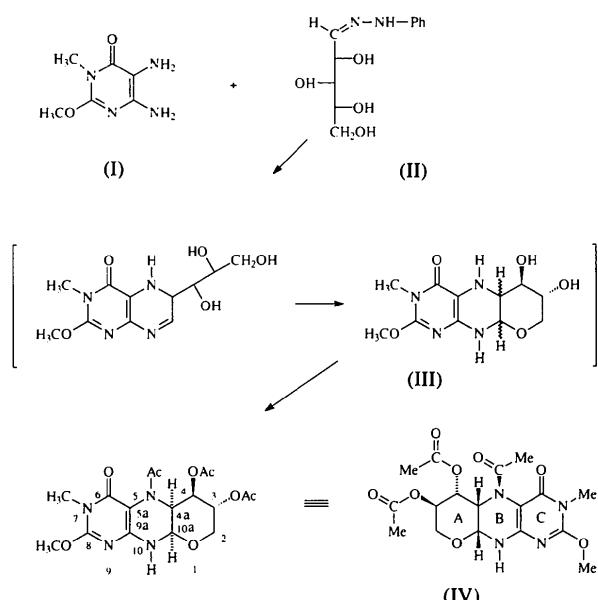
The bond lengths and angles are entirely in accord with those expected for this type of molecule (Orpen *et al.*, 1994) and serve to establish the structure

unequivocally, with *cis* H atoms at the *A/B* ring fusion and double bonds at C5*A*=C9*A* and C8=N9 (Table 2). It was not possible to establish the absolute structure of (IV) from the X-ray data, but this was already known from the configuration of the D-xylose used in its synthesis; Fig. 1 and the various data tables all refer to this known configuration. Ring *A* has a chair conformation (Boeyens, 1978) with the following Cremer & Pople (1975) parameters: puckering amplitude, $Q$ = 0.504 (5) Å, $\theta$ = 6.5 (6), $\varphi$ = 54 (5)°. The central *B* ring has a sofa conformation with N5 at the flap and $Q$ = 0.481 (5) Å, $\theta$ = 125.6 (6), $\varphi$ = 236.6 (7)°. The *C* ring is almost planar but is deformed slightly to a skew-boat conformation with $Q$ = 0.093 (5) Å, $\theta$ = 108 (3), $\varphi$ = 324 (3)°.
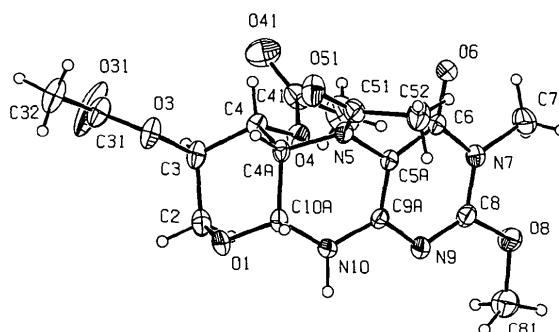


Fig. 1. A view of (IV) with the numbering scheme. Displacement ellipsoids are drawn at the 25% probability level.

In the crystal structure, molecules are linked to form infinite spirals about 2₁ screw axes along the *b* direction by N—H···O hydrogen bonds (Table 3). There are also a number of short C—H···O intramolecular interactions, as detailed in Table 3.

## Experimental

5,6-Diamino-2-methoxy-3-methylpyrimidin-4(3*H*)-one, (I), and D-xylose phenylhydrazone, (II), were reacted under the conditions described by Soyka, Pfleiderer & Prewo (1990). The pteridine product (III) was isolated in 52% yield and converted in 59% yield to its crystalline triacetyl derivative (IV) for crystal structure analysis.

*Crystal data*
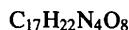
| | |
|---|---|
| C₁₇H₂₂N₄O₈ | Mo *Kα* radiation |
| $M_r$ = 410.38 | $\lambda$ = 0.71073 Å |
| Orthorhombic | Cell parameters from 25 |
| $P2_12_12_1$ | reflections |
| $a$ = 9.9075 (7) Å | $\theta$ = 12.50–20.00° |
| $b$ = 12.4566 (13) Å | $\mu$ = 0.10 mm⁻¹ |
| $c$ = 16.047 (2) Å | $T$ = 294 (1) K |
| $V$ = 1980.4 (4) Å³ | Block |
| $Z$ = 4 | 0.40 × 0.35 × 0.25 mm |
| $D_x$ = 1.376 Mg m⁻³ | Colourless |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 | $\theta_{max}$ = 26.86° |
| diffractometer | $h$ = 0 → 12 |
| $\theta/2\theta$ scans | $k$ = 0 → 15 |
| Absorption correction: | $l$ = 0 → 20 |
| none | 3 standard reflections |
| 2439 measured reflections | frequency: 120 min |
| 2439 independent reflections | intensity decay: 5.0% |
| 1515 observed reflections | |
| [$I > 3\sigma(I)$] | |

*Refinement*

| | |
|---|---|
| Refinement on $F$ | $(\Delta/\sigma)_{max}$ = 0.001 |
| $R$ = 0.042 | $\Delta\rho_{max}$ = 0.19 e Å⁻³ |
| $wR$ = 0.052 | $\Delta\rho_{min}$ = −0.18 e Å⁻³ |
| $S$ = 1.37 | Extinction correction: none |
| 1515 reflections | Atomic scattering factors |
| 262 parameters | from *International Tables* |
| H atoms riding; C—H, | *for X-ray Crystallography* |
| N—H = 0.95 Å | (1974, Vol. IV, Table |
| $w$ = 1/[$\sigma^2(F)$ + 0.0008$F^2$] | 2.2B) |

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.9630 (3) | 0.1410 (3) | 0.04407 (18) | 0.0429 (18) |
| O3 | 0.9458 (3) | 0.3460 (3) | −0.04038 (19) | 0.0491 (19) |
| O4 | 1.1196 (3) | 0.3538 (3) | 0.15859 (19) | 0.0416 (17) |
| O6 | 0.9345 (4) | 0.4172 (2) | 0.36959 (18) | 0.0471 (18) |
| O8 | 1.2417 (4) | 0.1625 (3) | 0.4361 (2) | 0.058 (2) |
| O31 | 1.0930 (5) | 0.4264 (6) | −0.1211 (3) | 0.130 (5) |
| O41 | 1.1768 (4) | 0.5208 (3) | 0.1193 (3) | 0.077 (3) |
| O51 | 0.6379 (3) | 0.3422 (4) | 0.1879 (2) | 0.063 (2) |
| N5 | 0.8525 (4) | 0.3026 (3) | 0.2236 (2) | 0.0347 (19) |
| N7 | 1.0929 (5) | 0.2895 (3) | 0.3989 (2) | 0.044 (2) |
| N9 | 1.1236 (4) | 0.1370 (3) | 0.3138 (2) | 0.0367 (19) |
| N10 | 1.0116 (4) | 0.1264 (3) | 0.1882 (2) | 0.0352 (19) |
| C2 | 1.0771 (5) | 0.2024 (5) | 0.0182 (3) | 0.050 (3) |
| C3 | 1.0511 (5) | 0.3204 (4) | 0.0190 (3) | 0.043 (3) |
| C4 | 1.0026 (5) | 0.3578 (4) | 0.1043 (3) | 0.037 (2) |
| C4a | 0.8912 (4) | 0.2857 (3) | 0.1363 (2) | 0.031 (2) |
| C5a | 0.9494 (5) | 0.2651 (4) | 0.2823 (2) | 0.033 (2) |
| C6 | 0.9871 (5) | 0.3307 (4) | 0.3506 (2) | 0.037 (2) |
| C7 | 1.1429 (8) | 0.3554 (5) | 0.4689 (3) | 0.070 (4) |
| C8 | 1.1506 (5) | 0.1939 (4) | 0.3795 (3) | 0.041 (3) |
| C9a | 1.0259 (4) | 0.1765 (3) | 0.2621 (2) | 0.031 (2) |
| C10a | 0.9175 (5) | 0.1649 (4) | 0.1253 (3) | 0.036 (2) |
| C31 | 0.9808 (5) | 0.3978 (5) | −0.1092 (3) | 0.054 (3) |
| C32 | 0.8691 (6) | 0.4114 (6) | −0.1687 (3) | 0.071 (4) |
| C41 | 1.1998 (6) | 0.4422 (5) | 0.1604 (3) | 0.052 (3) |
| C42 | 1.3146 (7) | 0.4249 (7) | 0.2190 (5) | 0.088 (5) |
| C51 | 0.7178 (5) | 0.3143 (4) | 0.2411 (3) | 0.042 (3) |
| C52 | 0.6733 (6) | 0.2883 (5) | 0.3285 (3) | 0.058 (3) |
| C81 | 1.3087 (6) | 0.0620 (5) | 0.4212 (4) | 0.066 (4) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| O1—C2 | 1.426 (7) | N7—C8 | 1.358 (6) |
| O1—C10a | 1.411 (5) | N9—C8 | 1.298 (6) |
| O3—C3 | 1.448 (5) | N9—C9a | 1.366 (6) |
| O4—C4 | 1.451 (5) | N10—C9a | 1.348 (5) |
| O6—C6 | 1.236 (6) | N10—C10a | 1.455 (6) |
| O8—C8 | 1.339 (6) | C2—C3 | 1.492 (8) |
| O8—C81 | 1.437 (7) | C3—C4 | 1.524 (6) |
| N5—C4a | 1.467 (5) | C4—C4a | 1.513 (6) |
| N5—C5a | 1.424 (6) | C4a—C10a | 1.538 (6) |
| N5—C51 | 1.372 (6) | C5a—C6 | 1.417 (6) |
| N7—C6 | 1.402 (6) | C5a—C9a | 1.377 (6) |
| N7—C7 | 1.477 (6) | | |

| | | | |
|---|---|---|---|
| C2—O1—C10a | 114.1 (3) | N5—C4a—C4 | 115.5 (4) |
| C3—O3—C31 | 117.8 (4) | N5—C4a—C10a | 107.1 (3) |
| C4—O4—C41 | 116.9 (4) | C4—C4a—C10a | 114.7 (4) |
| C8—O8—C81 | 116.9 (4) | N5—C5a—C6 | 120.0 (4) |
| C4a—N5—C5a | 114.1 (3) | N5—C5a—C9a | 118.6 (4) |
| C4a—N5—C51 | 117.8 (4) | C6—C5a—C9a | 119.9 (4) |
| C5a—N5—C51 | 123.7 (4) | O6—C6—N7 | 119.9 (4) |
| C6—N7—C7 | 117.9 (4) | O6—C6—C5a | 125.7 (4) |
| C6—N7—C8 | 120.6 (4) | N7—C6—C5a | 114.5 (4) |
| C7—N7—C8 | 121.4 (4) | O8—C8—N7 | 112.6 (4) |
| C8—N9—C9a | 116.2 (4) | O8—C8—N9 | 122.1 (4) |
| C9a—N10—C10a | 121.6 (4) | N7—C8—N9 | 125.4 (4) |
| O1—C2—C3 | 112.9 (4) | N9—C9a—N10 | 116.2 (4) |
| O3—C3—C2 | 109.6 (4) | N9—C9a—C5a | 122.4 (4) |
| O3—C3—C4 | 107.2 (4) | N10—C9a—C5a | 121.4 (4) |
| C2—C3—C4 | 111.3 (4) | O1—C10a—N10 | 111.5 (4) |
| O4—C4—C3 | 106.1 (4) | O1—C10a—C4a | 111.5 (3) |
| O4—C4—C4a | 111.0 (3) | N10—C10a—C4a | 110.6 (3) |
| C3—C4—C4a | 110.7 (4) | | |
| | | | |
| C9a—N9—C8—N7 | −2.0 (4) | C4—C4a—C10a—O1 | −47.1 (5) |
| N5—C4a—C10a—N10 | −52.0 (5) | | |

Table 3. *Hydrogen-bonding geometry* (Å, °)

| D—H···a | H···A | D···A | D—H···A |
|---|---|---|---|
| N10—H10···O6[i] | 1.99 | 2.816 (5) | 145 |
| C3—H3···O31 | 2.23 | 2.640 (7) | 105 |
| C4a—H4a···O51 | 2.26 | 2.735 (5) | 110 |
| C7—H7a···O8 | 2.19 | 2.647 (7) | 109 |

Symmetry code: (i) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Fig. 1 was prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1994a). An examination of the structure with the *SOLV* option in *PLATON* showed that there is a void in the asymmetric unit of volume 16.1 Å³ immediately adjacent to the carbonyl O31 atom and it is consequently not surprising that the *ORTEP*II plot shows that this atom is markedly anisotropic.

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# S-Methyl (2R,6S,8S)-2,6-Dimethoxy-4-methyl-3,5-dioxatricyclo[5.2.1.0^{4,9}]decane-8-thioate

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## Abstract

The X-ray analysis of the title compound, $C_{13}H_{20}O_5S$, confirms the *trans* relationship between the two methoxy groups on atoms C(2) and C(6) of the heterocyclic cage. The torsion angles C(15)—S—C(14)—O(8) and C(9)—C(8)—C(14)—O(8) have values of 0.0 (2) and −15.9 (3)°, respectively.

## Comment

The synthesis and chemistry of heterocyclic cage compounds has received attention in recent years (Metha & Reddy, 1987; Marchand, Reddy, Watson & Kashyap, 1990). The main motivation for these studies has been the desire to compare the reactivity pattern of carbon-cage compounds with their heteroatomic analogues. The synthesis of novel heterocyclic cage compounds by ozonolysis of thioesters followed by reduction with dimethyl sulfide was accomplished by Wu, Huang & Lin (1991). While seeking a protic solvent to improve the heterocyclic cage compound formation, the Diels–Alder