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ABSOLUTE CONFIGURATION OF TETRAPHYLLIN B, A CYANOGLUCOSIDE FROM *TETRAPATHAEA TETRANDRA*

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Key Word Index—*Tetrapathaea tetrandra*, Passifloraceae, tetraphillin B, cyanoglucoside, absolute configuration, X-ray crystal analysis

Abstract—The absolute configuration of tetraphyllin B, the major cyanoglucoside from immature fruit of *Tetrapathaea tetrandra*, was determined by X-ray diffraction and enzymic hydrolysis to be (1*S*,4*S*)-1-cyano-4-hydroxypent-2-en-β-D-glucoside

INTRODUCTION

From the immature fruit of the vine *Tetrapathaea tetrandra* Cheeseman, Passifloraceae, two cyclopentenyl cyanoglucosides have been isolated [1] and their structures determined by spectroscopic methods The major compound was tetraphyllin B (**1**) which has subsequently been found to occur in several other plants [2–5], often together with its epimer or as a 4-sulphate More recently the foliage of *T tetrandra* was also shown to contain an epimeric mixture of tetraphyllins A and B [6], although the immature fruit appeared to give chirally pure material [1] Since pairs of the C-1 epimers [2] of these cyanogens are now known to occur, even within the same plant, it has become important to determine their relative configurations The basic structures are known for the five cyclopentenyl cyanoglucosides but the overall stereochemistry has only been determined for gynocardin [7]

We wish to report that as a result of X-ray diffraction studies on crystals of tetraphyllin B, previously isolated from fruit of *T tetrandra*, this compound can be represented as (1*S*,4*S*)-1-cyano-4-hydroxypent-2-en-β-D-glucoside

RESULTS AND DISCUSSION

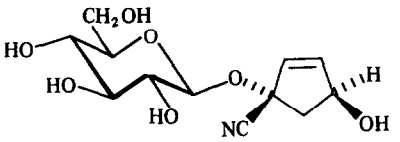
The material selected for X-ray diffraction was recrystallized from methanol–ethyl acetate, mp 170°, $[\alpha]_D^{20}$

Table 1 Fractional atomic co-ordinates* and thermal parameters† of tetraphyllin B

Atom	*x*	*y*	*z*	U_{eq}
O1′	−0 0183 (2)	0 1905 (1)	1 0795 (4)	0 029
O2′	0 2100 (2)	0 1201 (1)	1 0695 (4)	0 038
O3′	0 1946 (2)	−0 0122 (1)	0 8268 (4)	0 034
O4′	0 0641 (2)	0 0030 (1)	0 4455 (4)	0 033
O5′	−0 0735 (2)	0 1400 (1)	0 7723 (3)	0 028
O6′	−0 2427 (2)	0 0514 (1)	0 5443 (4)	0 036
O4	0 1445 (2)	0 4190 (1)	1 0887 (5)	0 044
N6	−0 1815 (3)	0 2925 (2)	1 3728 (5)	0 061
C1′	0 0302 (3)	0 1590 (2)	0 8980 (5)	0 026
C2′	0 1046 (3)	0 0950 (2)	0 9624 (6)	0 025
C3′	0 1393 (3)	0 0529 (2)	0 7679 (6)	0 024
C4′	0 0270 (3)	0 0374 (2)	0 6352 (5)	0 025
C5′	−0 0384 (3)	0 1059 (2)	0 5804 (5)	0 025
C6′	−0 1535 (3)	0 0965 (2)	0 4497 (6)	0 031
C1	−0 0135 (3)	0 2660 (2)	1 0885 (6)	0 027
C2	−0 0355 (3)	0 3026 (2)	0 8798 (5)	0 028
C3	0 0542 (3)	0 3457 (2)	0 8318 (6)	0 033
C4	0 1510 (4)	0 3502 (2)	0 9988 (6)	0 032
C5	0 1156 (4)	0 2924 (2)	1 1568 (7)	0 038
C6	−0 1100 (4)	0 2820 (2)	1 2473 (6)	0 036

*Standard deviations, given in parentheses, are based on least-squares parameters

†$U_{eq} = \frac{1}{3}\Sigma\Sigma U_{ij} a_i^* a_j^* (\bar{a}_i \cdot \bar{a}_j)$



1

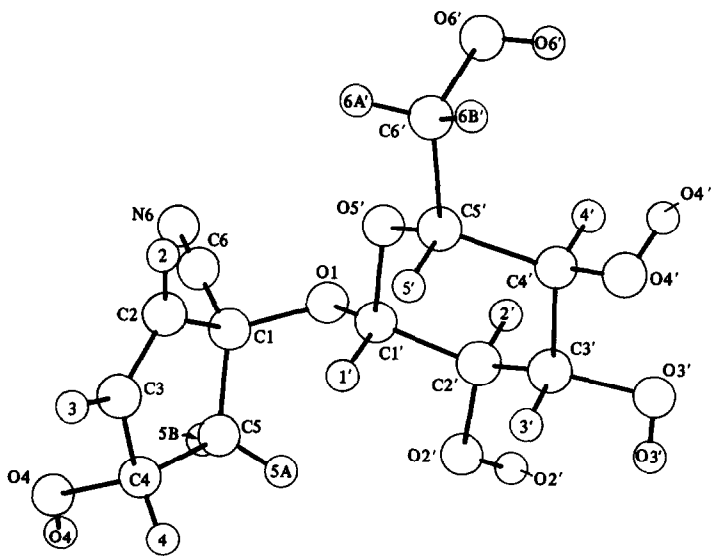
$-35\,6°$ (H_2O) Tetraphyllin B crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 10\,8446\ (18)$ Å, $b = 19\,1487\ (29)$ Å and $c = 6\,3401\ (9)$ Å Densities observed 1 45 (1) by density bottle, with four molecules/unit cell, calculated, 1 45 g/cm^3

A total of 1882 independent reflections were collected on a Nicolet R3M automatic diffractometer using MoKα radiation and a graphite monochromator within the limits $3° < 2\theta < 56°$ The structure was solved using the random phase refinement programme RANT in SHELXTL [8] Of the 20 nonhydrogen atoms in the asymetric unit, 19 were located in the E-map with the highest figure of merit using the 547 E values $> 1\,2$ Full matrix least squares refinement [9] minimising the function $\Sigma w(F_o/-/F_c)^2$ was performed All 17 hydrogen atoms were found in subsequent difference Fourier maps calculated at intermediate stages in the refinement All non-hydrogen and hydrogen atoms were refined with anisotropic and isotropic thermal parameters, respectively Coordinates and U_{eq} values for the non-hydrogen atoms are given in Table 1, Table 2 contains the bond distances and angles for these atoms Anisotropic thermal parameters for the non-hydrogen atoms, hydrogen coordinates and their U's,

Table 2 Interatomic distances (Å) and angles (°) of tetraphyllin B

O1′–C1′	1 401 (4)	C1–O1′–C1′	116 6 (3)
O2′–C2′	1 413 (4)	O5′–C1′–O1′	105 8 (2)
O4′–C4′	1 430 (4)	C2′–C1′–O5′	111 3 (2)
O5′–C5′	1 432 (4)	C3′–C2′–O2′	111 7 (3)
O4–C4	1 438 (4)	C2′–C3′–O3′	110 7 (3)
C1′–C2′	1 522 (4)	C4′–C3′–C2′	110 8 (3)
C3′–C4′	1 510 (4)	C5′–C4′–O4′	109 6 (3)
C5′–C6′	1 509 (5)	C4′–C5′–O5′	108 7 (3)
C1–C5	1 550 (5)	C6′–C5′–C4′	114 0 (3)
C2–C3	1 313 (5)	C2–C1–O1′	114 9 (3)
C4–C5	1 542 (5)	C5–C1–C2	103 7 (3)
O1′–C1	1 449 (3)	C6–C1–C2	112 7 (3)
O3′–C3′	1 432 (4)	C3–C2–C1	112 1 (3)
O5′–C1′	1 426 (3)	C3–C4–O4	107 5 (3)
O6′–C6′	1 429 (4)	C5–C4–C3	104 1 (3)
N6–C6	1 129 (4)	C1–C6–N6	177 5 (4)
C2′–C3′	1 521 (4)	C5′–O5′–C1′	112 4 (2)
C4′–C5′	1 530 (4)	C2′–C1′–O1′	109 0 (3)
C1–C2	1 515 (5)	C1′–C2′–O2′	106 5 (3)
C1–C6	1 484 (5)	C3′–C2′–C1′	109 9 (3)
C3–C4	1 493 (5)	C4′–C3′–O3′	108 2 (3)
		C3′–C4′–O4′	109 3 (3)
		C5′–C4′–C3′	109 4 (3)
		C6′–C5′–O5′	107 5 (3)
		C5′–C6′–O6′	113 6 (3)
		C5–C1–O1′	111 6 (3)
		C6–C1–O1′	102 0 (3)
		C6–C1–C5	112 3 (3)
		C4–C3–C2	113 2 (3)
		C5–C4–O4	112 9 (3)
		C4–C5–C1	106 1 (3)

Standard deviations, given in parentheses, are based on least squares parameters



2

H atoms are shown as small circles with included figures

other bond distances and angles and listings of the final structure factors are available*

The final results of the X-ray diffraction analysis is illustrated by the computer generated [14] structure **2** for tetraphyllin B Although the absolute configuration was not determined from the diffraction study it can be inferred from the β-D-glucose moiety which was identified after enzymic hydrolysis [1] The configuration at C1 and C4 of the cyclopentene ring can both be represented as *S*

The glucose moiety demonstrates all the features previously noted in studies of β-pyranosides [10], shortening of C5′–C6′ to 1 509 (5) Å compared with the interring mean of 1 521 Å, anomeric shortening of C1′–O1′ compared with C1′–O5′ and C5′–O5′, enlarged C4′–C5′–C6′ angle at the expense of O5′–C5′–C6′ and a mean torsion angle of 57 4° [11] The mean C–O bond length is normal at 1 429 (8) Å The average deviation of atoms from the three least squares planes through opposite bonds (0 019, 0 008, 0 030 Å) and the torsion angles, indicate a slightly distorted chair conformation

The bond lengths and angles for the cyanocyclopentenyl moiety are consistent to those found for a similar structure [12] The cyclopentenyl ring has a flattened envelope conformation with C5 0 14 Å from the plane of the other atoms (mean deviation is 0 011 Å) The mean O–H bond length (0 81 Å) is normal (0 78 Å [10]) The torsion angles characterising the glycosidic linkages (O5′–C1′–O1′–C1 and C1′–O1′–C1–C5) are 102 2° and 80 7° which are significantly different from those of methyl β-pyranosides [13] The cyano group at C1 seems to be the most likely cause for this change

The cyano group at C1 of tetraphyllin in *cis* to the hydroxyl at C4 in contrast to gynocardin where these two groups are in a *trans* relationship since gynocardin is 1*S*, 4*R* [7] Since tetraphyllin B can be represented by **1** and **2**, epitetraphyllin B which has been shown to be epimeric at C1 [2] can be represented by the *R* configuration at this atom Tetraphyllin A probably has the same configuration as tetraphyllin B at C1

*Data available on request from Dr G J Gainsford, Chemistry Division, DSIR, Private Bag, Petone, New Zealand

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