# Crystal and molecular structure of methyl $\alpha$ -D-galactopyranoside 4-(sodium sulphate) dihydrate

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(Received July 14th, 1990; accepted for publication, September 24th, 1990)

## ABSTRACT

The crystal and molecular structure of methyl  $\alpha$ -D-galactopyranoside 4-(sodium sulphate) dihydrate has been determined by X-ray analysis at  $-173^{\circ}$ . The sugar ring has a distorted  ${}^{4}C_{1}$  chair conformation. The conformation of the CH<sub>2</sub>OH group is *gauche-trans* and the bridging S-O bond is eclipsed with the C-4-H bond, which diminishes the steric repulsion of the sulphate group with the neighbouring CH<sub>2</sub>OH and HO-3 groups. The sodium ions occupy special positions on two-fold axes and each is co-ordinated six-fold. The three independent oxygen atoms around Na-1 belong to two different sulphate oxygen atoms that are associated with two different sugar rings and O-3 of one of these rings. In the co-ordination of Na-2, the three independent oxygen atoms belong to one of the water molecules and one sulphate group. The co-ordination of Na-1 approaches ideal octahedral symmetry, whereas that of Na-2 is distorted appreciably. Both the co-ordination and hydrogen bonding result in a complex packing pattern in which the single hydrogenbonded helix around the screw is axis involves the hydroxymethyl group and a water molecule, and is almost identical to the arrangement observed for methyl  $\alpha$ -D-galactopyranoside monohydrate.

## INTRODUCTION

Although the occurrence of sulphated carbohydrates in Nature is widespread, little is known about their molecular structures. There have been several studies of the positions of the sulphate groups in polysaccharides, especially in sulphated galactans<sup>1</sup>. Galactans have repeating units of 3-linked  $\beta$ -D-galactopyranose residues (A units) and 4-linked  $\alpha$ -(D- or L-)galactopyranose residues (B units). The gelling properties<sup>2</sup> of galactans have been studied, as has the role of the sulphate groups as antigenic determinants<sup>3</sup>. The formation of gels probably involves double-helical polysaccharide chains<sup>4-6</sup> and the role of sulphate groups may be important<sup>7,8</sup>. Non-specific competition for water by counter ions may be the trigger that increases the interaction of the polysaccharide chains and results in the formation of the gel network<sup>9</sup>.

Important information on stereochemistry can be obtained by X-ray crystallographic studies of simple model compounds such as sulphated pyranosides. It is of particular interest to unravel the network of hydrogen bonds and the co-ordination of cations, which undoubtedly play a vital role in the control of the conformation of a

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polymer chain. Also, accurate structural information is necessary for force-field calculations on sulphated carbohydrates.

The crystal and molecular structures of  $\beta$ -D-glucopyranose 6-(potassium sulphate)<sup>10</sup> (2) and sucrose octasulphate<sup>11</sup> have been described, and now we report on methyl  $\alpha$ -D-galactopyranoside 4-(sodium sulphate) dihydrate (1).

## EXPERIMENTAL

Compound 1, synthesised by Contreras *et al.*<sup>12</sup>, had m.p. 190–191° and  $[\alpha]_D + 116°$  (*c* 1.4, water), and suitable crystals were grown by the vapour-phase diffusion method with methanol as solvent and butyl acetate as the precipitant.

A needle-shaped crystal  $(0.9 \times 0.1 \times 0.1 \text{ mm})$  was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a liquid nitrogen cooling device, and Zr-filtered Mo- $K_{\alpha}$  radiation ( $\lambda 0.71073$ Å) was used. The lattice dimensions were determined by refining the setting angles of 25 reflections in the  $\theta$  range of 9–13°. Systematic absences hkl with h + k = 2n + 1, together with the chirality of 1, indicated the space group C2. The crystal data are given in Table I.

Within one quarter of the reflection sphere, 1857 unique reflections were measured up to  $2\theta_{max} = 55^{\circ} [h, 0-37; k 0-7; l - 10-10]$  with the  $\omega/2\theta$  scan method,  $\omega = [0.60 + 0.35 \tan\theta]$ , of which 1471 were above the  $2.5\sigma(I)$  level. The variation in intensity was monitored with two periodically measured standard reflections (401 and 110). The r.m.s. deviation amounted to 3.0 and 1.4%, respectively, during exposure to X-rays for 30 h. Calculation of the variance  $\sigma^2(I)$  was based on counting statistics plus a term (pI) where p = 0.02 is the instability constant<sup>13</sup>.

After corrections for instability and Lp, the structure was solved by direct methods with the SHELXS-86 program<sup>14</sup>, which gave all of the non-H atoms. The

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Crystal data for methyl  $\alpha$ -D-galactopyranoside 4-(sodium sulphate) dihydrate (1)

Molecular formula	$(C_7H_1,O_8S)^-Na^+\cdot 2H_2O$	
Molecular weight	332.29	
Crystal system	Monoclinic	
Space group	C2	
Cell dimensions		
a (Å)	28.618(5)	
b (Å)	5.7999(15)	
c (Å)	7.9828(10)	
β (°)	99.390(12)	
Cell volume (Å <sup>3</sup> )	1307.2(4)	
Ζ	4	
F(000)	696 -	
$\mu \left( \text{Mo-}K_{\alpha} \right) \left( \text{cm}^{-1} \right)$	3.2	
$D_{\rm c} ({\rm g.cm^{-3}})$	1.688	
Temperature (K)	100	

aliphatic H atoms were placed at ideal sp<sup>3</sup> positions (C-H 1.08Å) and refined in the riding mode. The methyl group was treated as a rigid group.

After anisotropic full-matrix refinement of non-H atoms with the SHELX-76 program<sup>15</sup>, the difference synthesis revealed the position of the H atoms of the hydroxyl groups and the water molecules. However, the positional refinement of the H atoms resulted in unrealistic geometries and, therefore, these atoms were constrained during refinement at the maxima of the difference Fourier map.

The final refinement with 185 parameters, including scale factor, positional, and anisotropic thermal parameters of the non-H atoms and a general isotropic temperature factor of the H atoms, converged to R = 0.043,  $R_w = 0.048$ , with  $w = \sigma^2 (F_o)^{-1}$  based on counting statistics, and S = 1.62. The general isotropic thermal parameter of the H atoms was refined to 0.03  $Å^2$ . The average and maximum shift-to-error ratios were 0.025 and 0.111, respectively, and the final difference map showed minimum and maximum peaks of -0.59 and 0.46 eÅ<sup>-3</sup>. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography<sup>16</sup>. All geometric calculations and illustrations were performed with the EUCLID package<sup>17</sup>.

Final atomic co-ordinates of non H-atoms are listed in Table II, the description of

Atomic positional and thermal parameters					
Atom	x/a	y/b	z/c	U <sub>eq</sub> <sup>a</sup>	
S	0.03209(3)	0.5129(-)	0.7516(1)	0.0090(3)	
Na-1	0(-)	0.9991(6)	0.5(-)	0.0116(7)	
Na-2	0(-)	0.8341(5)	0(-)	0.0168(8)	
O-1	0.1964(1)	0.5352(7)	0.3815(4)	0.0128(9)	
O-2	0.1292(1)	0.8072(7)	0.2335(4)	0.016(1)	
O-3	0.0831(1)	0.9708(6)	0.5113(4)	0.0130(9)	
0-4	0.07083(9)	0.5068(7)	0.6329(3)	0.0105(8)	
O-5	0.1473(1)	0.3276(6)	0.5302(4)	0.0110(9)	
O-6	0.1996(1)	0.1604(7)	0.8390(4)	0.019(1)	
0-7	0.0047(1)	0.3095(7)	0.6978(4)	0.014(1)	
<b>O-8</b>	0.0052(1)	0.7255(6)	0.7172(4)	0.012(1)	
0-9	0.0558(1)	0.5051(8)	0.9265(3)	0.0132(8)	
O-10	0.0566(1)	0.1039(7)	0.1078(4)	0.016(1)	
0-11	0.2051(1)	0.8036(7)	0.0502(4)	0.022(1)	
C-1	0.1503(2)	0.4585(8)	0.3804(5)	0.010(1)	
C-2	0.1168(2)	0.6651(9)	0.3640(5)	0.010(1)	
C-3	0.1195(2)	0.7996(9)	0.5295(5)	0.013(1)	
C-4	0.1151(2)	0.6371(9)	0.6748(5)	0.010(1)	
C-5	0.1552(2)	0.4594(8)	0.6847(5)	0.011(1)	
C-6	0.1581(2)	0.296(1)	0.8348(6)	0.015(1)	
C-7	0.2286(2)	0.352(1)	0.3670(7)	0.025(2)	

## TABLE II

<sup>a</sup>  $U_{eq} = 1/3 \sum_{i} \sum_{j} U_{ij} \mathbf{a}_{i}^{*} \mathbf{a}_{j}^{*} \mathbf{a}_{i} \mathbf{a}_{j}$ 

## TABLE III

Internal geomet	ry of 1	····			
Bond distances (	(Å)			<u></u>	
SO-4	1.572(3)		O-5-C-1	1.431(5)	
SO-7	1.442(4)		0-5-C-5	1.437(5)	
SO-8	1.455(4)		O-6-C-6	1.419(6)	
SO-9	1.450(3)		C-1-C-2	1.527(7)	
O-1-C-1	1.391(5)		C-2-C-3	1.525(6)	
0-1-C-7	1.422(7)		C-3-C-4	1.516(6)	
O-2-C-2	1.418(6)		C-4-C-5	1.534(7)	
O-3-C-3	1.430(6)		C-5-C-6	1.520(7)	
<u>0-4-C-4</u>	1.467(6)				
Bond angles (de	grees)				
<b>O-4-5-0-</b> 7	101.8(2)		0-2-C-2-C-3	110.8(4)	
O-4-S-O-8	107.9(2)		C-1C-2C-3	112.6(3)	
0-4-S-0-9	108.3(2)		O-3-C-3-C-2	109.5(3)	
O-7–S–O-8	113.1(2)		0-3-C-3-C-4	111.0(4)	
O-7-S-O-9	114.1(2)		C-2C-3C-4	110.2(4)	
O-8-S-O-9	111.0(2)		O-4-C-4-C-3	108.8(3)	
S-0-4-C-4	121.3(3)		0-4-C-4-C-5	106.0(4)	
C-1-O-1-C-7	112.8(4)		C-3-C-4-C-5	107.6(3)	
C-1-O-5-C-5	114.4(3)		O-5-C-5-C-4	107.6(3)	
0-1-C-1-O-5	110.5(3)		O-5-C-5-C-6	109.0(4)	
0-1-C-1-C-2	109.4(4)		C-4-C-5-C-6	113.9(4)	
O-5-C-1-C-2	111.5(3)		O-6-C-6-C-5	107.6(4)	
0-2-C-2-C-1	106.9(3)				, <u>, , , , , , , , , , , , , , , , ,</u>
Bonds and angle	s involving h	ydrogen atoms			
Type		Number	Mean	σ	Range
O-H (incl. wate	r)	7	0.91 Å	0.009 Å	0.78–1.04 Å
С-О-Н	,	3	101°	4°	98.2-106.1°
H-O-w-H		2	101.8°	2.8°	<b>99.3</b> –103°
		· · · · · · · · · · · · · · · · · · ·			

the internal geometry is shown in Table III, and the co-ordination of the sodium ions and the hydrogen-bond geometry are given in Tables IV and V, respectively\*.

## **RESULTS AND DISCUSSION**

Molecular geometry. — A perspective view of 1 together with the numbering scheme is presented in Fig. 1. The C–C and hydroxylic C–O bond lengths range from 1.516 (6) to 1.534(7) Å and 1.418(6) to 1.430(6) Å, respectively, and their values are

<sup>\*</sup> The observed and calculated structure factors, H atom co-ordinates, and anisotropic thermal parameters of the non-H atoms have been deposited with, and may be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/459/Carbohydr. Res., 212(1991) 1-11.

#### TABEL III (continued)

Torsion angles (degrees)		
Endocyclic		
O-5-C-1-C-2-C-3	46.5(5)	
C-1-C-2-C-3-C-4	-50.0(5)	
C-2-C-3-C-4-C-5	58.2(5)	
C-3-C-4-C-5-O-5	-64.1(4)	
C-4-C-5-O-5-C-1	64.1(4)	
C-5-O-5-C-1-C-2	- 54.9(5)	
Exocyclic		
C-7-O-1-C-1-C-2	-169.8(4)	
C-7-O-1-C-1-O-5	67.1(5)	
O-1-C-1-O-5-C-5	66.9(5)	
O-1-C-1-C-2-C-3	-76.0(4)	
O-6-C-6-C-5-C-4	-173.4(4)	
O-6-C-6-C-5-O-5	66.5(5)	
C-6-C-5-O-5-C-1	-171.9(3)	
C-6C-5C-4C-3	175.0(4)	
O-1-C-1-C-2-O-2	45.9(4)	
O-2-C-2-C-1-O-5	168.4(3)	
O-2-C-2-C-3-C-4	-169.7(4)	
O-2-C-2-C-3-O-3	67.9(5)	
O-3-C-3-C-4-C-5	179.7(4)	
O-3-C-3-C-2-C-1	-172.5(4)	
SO-4C-4H-4	0.6(6)	
O-4-C-4-C-3-O-3	65.3(5)	
O-4-C-4-C-3-C-2	- 56.3(5)	
O-4-C-4-C-5-O-5	52.2(4)	
O-4-C-4-C-5-C-6	- <b>68</b> .7(4)	
S-O-4-C-4-C-3	-122.5(3)	
S-O-4-C-4-C-5	122.0(3)	
0-7	-160.9(3)	
O-8-S-O-4-C-4	79.8(4)	
0-9-5-0-4-C-4	- 40.4(4)	

within the ranges reported for other carbohydrates<sup>18,19</sup>. The commonly observed difference between the endocyclic C-1–O-5 and C-5–O-5 distances, due to the anomeric effect, is absent (see Table III). However, the shortening of the C-1–O-1 bond is larger than that in  $\alpha$ -D-pyranosides<sup>18</sup>.

In the sulphate group, the bridging S–O distance is long [1.572(3)Å] and the three other S–O distances [av. 1.449 Å] are equal within the  $3\sigma$  range and are in between the non-bridging S–O values found in SO<sub>4</sub><sup>2–</sup> [av. 1.472(13)Å] and C–SO<sub>2</sub>–O–C [av. 1.423 (8)Å]<sup>18</sup>. In contrast, the structure of  $\beta$ -D-glucopyranose 6-(potassium sulphate) (2) showed three S–O distances that range from 1.414(4) to 1.451(5)Å, whereas the bridging S–O distance was similar [1.563(4)Å] to that of 1. The C-4–O-4 bond in 1 was 1.467(6)Å and this lengthening, which is also present in C-6–O-6 of 2 [1.472(7)Å], is caused apparently by sulphation of O-4.

## TABLE IV

Symmetry code					
a x b x c x d x	y z $1+y z$ $-1+y 1+z$ $y -1+z$	e f g h	$\begin{array}{cccccccc} -x & 1+y & 1-z \\ 1/2-x & 1/2+y & 1-z \\ -x & y & 1-z \\ -x & 1+y & -z \end{array}$		
Туре	Bond length (Å)	Туре	Bond angle (°)		
Na-1····O-3 <sup>a</sup> 2.372(3) Na-1····O-7 <sup>b</sup> 2.384(5)		$O-3^{a}-Na-1-O-3^{g}$ $O-7^{b}-Na-1-O-8^{g}$	172.10(20) 173.72(17)		
Na-1O-9	2.337(4)	$\begin{array}{c} O-8^{g}\cdots Na-1\cdots O-8^{a}\\ O-8^{g}\cdots Na-1\cdots O-3^{a}\\ O-8^{g}\cdots Na-1\cdots O-3^{g}\\ O-8^{g}\cdots Na-1\cdots O-7^{c}\\ O-3^{a}\cdots Na-1\cdots O-7^{c}\\ O-3^{a}\cdots Na-1\cdots O-7^{b}\\ O-7^{b}\cdots Na-1\cdots O-7^{c}\\ \end{array}$	94.47(17) 85.63(13) 88.98(13) 91.81(12) 91.47(14) 94.52(14) 81.92(16)		
Na-2····O-8 <sup>d</sup> Na-2····O-9 <sup>d</sup> Na-2····O-10 <sup>b</sup>	2.372(2) 2.616(4) 2.314(4)	$O-8^{d} \cdots Na-2 \cdots O-8^{g}$ $O-9^{d} \cdots Na-2 \cdots O-10^{h}$	149.21(18) 145.65(10)		
		$\begin{array}{c} O-10^{b} \cdots Na - 2 \cdots O-10^{h} \\ O-10^{b} \cdots Na - 2 \cdots O-8^{d} \\ O-10^{b} \cdots Na - 2 \cdots O-8^{g} \\ O-10^{b} \cdots Na - 2 \cdots O-9^{d} \\ O-8^{d} \cdots Na - 2 \cdots O-9^{d} \\ O-8^{d} \cdots Na - 2 \cdots O-9^{g} \\ O-9^{d} \cdots Na - 2 \cdots O-9^{g} \\ O-9^{d} \cdots Na - 2 \cdots O-9^{g} \end{array}$	94.90(17) 112.61(12) 88.54(12) 99.25(12) 57.12(11) 98.95(13) 86.34(15)		

# Geometry of the sodium co-ordination

## TABLE V

Geometry of the hydrogen-bonding pattern"

Donor-Hacceptor	$D \cdots A (\mathring{A})$	<b>O–H</b> (Å)	HO (Å)	<i>O−H</i> ···· <i>O</i> (°)
0-2-H-220-10 <sup>b</sup>	2.758(5)	0.96	1.84	160
Q-3-H-33Q-5 <sup>b</sup>	2.755(5)	0.82	1.96	165
<b>O-6-H-66</b> ····· <b>O-</b> 11°	2.658(5)	0.89	1.80	165
O-10-H-101O-9 <sup>d</sup>	2.739(6)	0.78	2.02	155
O-10-H-102O-7 <sup>g</sup>	2.792(5)	0.91	1.99	145
<b>O-11–H-111O-6</b> <sup>f</sup>	2.852(5)	1.04	1.88	155
O-11-H-112O-1ª	3.113(5)	0.97	2.34	135
O-11-H-112O-2ª	2.810(5)	0.97	1.94	150

" For the symmetry codes, see Table IV.



Fig. 1. Perspective view and atom labeling of methyl a-D-galactopyranoside 4-sulphate (1).

The bond angles (see Table III) are well within the range generally accepted for pyranoses. The O–S–O angles showed a wide range from 101.8(2) to  $114.1(2)^{\circ}$ , which compared satisfactorily with the range for 2 [102.7(2) to  $115.5(3)^{\circ}$ ].

The galactopyranose ring adopts a moderately distorted chair conformation as follows from the Cremer and Pople<sup>20</sup> puckering parameter  $\theta$  (11.9°). In 2, the chair is also distorted ( $\theta = 8.0^{\circ}$ ), whereas, in methyl  $\alpha$ -D-galactopyranoside hydrate<sup>21</sup> (3), the distortion is much less ( $\theta = 4.6^{\circ}$ ).

The conformation of the hydroxymethyl group in 1 is gauche-trans which, together with the trans-gauche conformation, is the preferred conformation in  $\alpha$ -D-galactopyranosides, as shown by a search of the Cambridge Structural Database<sup>22</sup>. The bridging S-O bond is eclipsed with the C-4-H-4 bond, which diminishes steric repulsion of the sulphate group with the CH<sub>2</sub>OH and HO-3 groups. For the same reason, the sulphate group deviates considerably (~20°) from the ideal staggered conformation with respect to the C-4-O-4 ester bond. The O-C bond of MeO-1 is oriented gauche-trans with respect to O-5 and C-2, respectively.

Co-ordination of the sodium ions. — The structure of 1 contains two independent sodium ions that occupy special positions on two-fold axes. Each ion has a six-fold oxygen co-ordination, which is octahedral for Na-1 and severely distorted octahedral for Na-2 (see Table IV and Fig. 2). The three oxygen atoms (O-3, O-7, and O-8) around Na-1 belong to two different pyranose residues. For Na-2, O-8 and O-9 are from one sulphate group and O-10 is from the water molecule. In 2, the co-ordination of the potassium ions is octahedral, whereas, in the complex  $\alpha$ -D-glucose·NaCl<sup>23</sup>, the octahedral co-ordination of sodium is distorted severely.

Crystal packing. — The packing of 1 is portrayed in Fig. 3, which shows a view along the b axis. The packing pattern is governed by co-ordination of the sodium ions and hydrogen bonds which result in a complex tight packing that consists essentially of



Fig. 2. View of a part of the structure of 1 along the a axis, which shows the linking of the Na-1 and Na-2 octahedrons and the role of the bridging water molecule O-10.

two symmetry-related layers in the *bc* planes at x = 0 and 1/2. Within each layer, co-ordination of the two sodium ions serves as a cohesive element, whereas hydrogen bonds formed by O-11 of water molecules occur between the layers (see Fig. 3). The galactopyranoside ring is almost parallel to the layer.

By sharing O-8 atoms within each layer, the sodium octahedrons form endless chains in the c direction and the O-10 water molecules link the octahedrons along the b and c axes (see Fig. 2). In the chain along the b axis, the water molecule O-10 is co-ordinated to the Na-2 octahedron and is a hydrogen-bond donor to sulphate O atoms (O-7 and O-9) of the neighbouring octahedron.

Hydrogen bonds. — All of the potential hydrogen-bond donors are involved in intermolecular hydrogen bonds (see Table V). With the exception of O-3, O-4, and O-8, all of the O atoms accept a hydrogen bond. The pyranose rings are stacked along the short b axis and are connected by HO-3…O-5 hydrogen bonds. Columns of four of these stacks around the two-fold axis are connected through the O-10 water molecules which, by donating two hydrogen bonds to symmetry-related sulphate groups, accepting an O-2–H bond, and co-ordinating to Na-2, constitute an important cohesive element along the b axis (see Fig. 3).

An interesting feature of the hydrogen-bond network concerns the water molecule O-11, which donates a single bond to O-6 and a bifurcated bond to O-1 and O-2 of neighbouring galactose molecules and accepts a hydrogen bond from HO-6 of a third galactose molecule (see Fig. 3). The  $2_1$  axis generates this pattern into an infinite hydrogen-bonded helix in the direction of the *b* axis.



Fig. 3. View of the unit cell of 1 along the b axis, which shows co-ordination of the sodium ions and the hydrogen bonds.



Fig. 4. Comparable packing pattern and hydrogen-bond helix as seen along the *a* axis in the structure of methyl  $\alpha$ -D-galactopyranoside monohydrate (3) [space group  $P2_12_12_1$  with a = 6.130(1), b = 7.486(1), and c = 21.202(3) Å].

## TABLE VI

generospytemotide monouydrate (5)					
1			3		
<u>D-H····A</u>	$\underline{D}\cdots A$ (Å	<u>) &lt;(0-H····0) (°</u>	) <b>D-H····</b> A	D····A (Å	) <(O-H····O) (°)
O-6–H····O-11°	2.658(5)	165	O-6–H····O-w	2.683(5)	165
O-11-H-111O-6 <sup>r</sup>	2.852(5)	155	O-w-H-15O-6	2.745(5)	155
O-11-H-112O-1ª	3.113(5)	135	O-w-H-16O-1	2.880(5)	130
O-11-H-112O-2ª	2.810(5)	150	O-w-H-16O-2	3.019(5)	135

Hydrogen bonds in the helix of methyl  $\alpha$ -D-galactopyranoside 4-(sodium sulphate) dihydrate (1) and methyl  $\alpha$ -D-galactopyranoside monohydrate (3)<sup>a</sup>

" For the symmetry codes, see Table IV.

A similar helical chain of hydrogen bonds is present in the structure of methyl  $\alpha$ -D-galactopyranoside hydrate<sup>21</sup> (3), but the handedness of the helices is reversed (see Fig. 4) and the bifurcated bonds in each structure, which are asymmetric in type<sup>24</sup>, differ in the asymmetry by reversal of the O-1 and O-2 acceptors (see Table VI). The general packing patterns of 1 and 3 also display similarities in the HO-3…O-5 interaction along the short *b* axis, as follows from a comparison of Fig. 3 and 4.

#### ACKNOWLEDGMENT

We thank Dr. A. L. Spek for his assistance in preparing the illustrations.

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