STRUCTURE OF A NEW CARBIDE OF TITANIUM

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IT seems likely that a new carbide, a bicarbide of titanium exists. The compound, interesting in that it has a very small unit cell, a simple cubic cell of side 3·13 Å, was discovered while the authors had occasion to examine the powder pictures of a material obtained when ethylene was treated with titanium tetrachloride at a fairly high temperature in a sealed quartz tube. The resultant product contained several phases of differing density of range 1·5 to 2·5. Powder photographs were taken of each fraction. The fractions of density less than 1·8 gave a set of sharp lines that could be indexed on the basis of a simple cubic cell of size 3·13 Å. The fraction had an admixture of free carbon and its true composition was difficult to assess, though the titanium content was 35%. Consequently, any relevant information had to be inferred from the powder photograph. The observed spacings and visually estimated intensities are given in Table I.

TABLE I

Intensity data for TiC_2. *Simple cubic with* $a = 3·13\ Å$

$\sin^2\theta$	Index	Intensities	
		Observed	Calculated
0·061	100	10	4533
0·120	110	15	8161
0·181	111	4	1836
0·242	200	2	1061
0·301	210	8	2223
0·360	211	6	1132
0·481	220	3	370
0·540	221	6	1527
0·598	310	4	1031
0·662	311	4	771
..	222	..	91
0·779	320	3	918
0·836	321	6	1503

Clearly the compound is not titanium because few elements have the simple cubic system. It is not TiC, which is of the NaCl type, face-centred cubic of size 4·32 Å with four molecules per cell. (In fact, TiC was detected in the fractions with higher density and higher titanium content.) The smallness of the cell allows not more than one molecule per cell and no structure could be proposed with one

Ti atom and one C atom per unit cell, which could explain the absence of the reflection 222. The mode of preparation of the substance demands that it is a compound of only titanium and carbon. It is reasonable to expect that the compound is TiC_2, if it cannot be TiC. Higher carbides are of course not possible because the cell is too small for them.

A structure based on one molecule per simple cubic unit cell of size 3·13 Å could be proposed provided a statistical arrangement of the C_2 group was allowed. There is only one C_2 group but the symmetry is cubic, so that it is necessary for the C_2 group to lie parallel to the three cubic axes with equal probability in different unit cells. The origin is chosen midway between the two carbon atoms and the titanium atom is placed at (1/2, 1/2, 1/2). The carbon atom is defined by a parameter u in the set of co-ordinates $(u, 0, 0 ; -u, 0, 0) ; (0, u, 0 ; 0, -u, 0) ; (0, 0, u ; 0, 0, -u)$. In a particular cell, the two carbon atoms would have one of these three pairs of co-ordinates. However, because of the statistical arrangement, there would be equal probability for all the three pairs, and consequently, the intensities were calculated assuming 1/3 of a carbon atom to be present at each of the six positions. The best agreement was found by trial and error to occur at $u = 0·25$. The intensities calculated for this value of u are also given in Table I and there is good agreement with observation. The agreement, however, is only qualitative. No quantitative measurements have been made in view of the heavy fluorescent radiation from titanium. Further, the compound itself is very unstable and breaks down in the presence of moisture. Because of these, a more detailed investigation seems difficult to undertake.

However, even the qualitative data are sufficient to bring out the correctness of the structure. The strongest of the calculated set are the strongest of the measured ones and the weakest, 222, is not at all observed on the photograph. On the basis of the above structure the Ti-C distance comes out to be 2·34 Å as against 2·2 Å for TiC. The C-C distance is found to be 1·56 Å. The occurrence of such C_2 groups in CaC_2 is well known where the C-C distance within the group is 1·53 Å. In view of these considerations, it is quite possible the higher carbide TiC_2 exists and has a

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statistical structure. The main interest is that this compound is one of the very few that are known to have such a small cubic unit cell. There exist some elements which have smaller cells than the one under discussion but to the best of the authors' knowledge there is no other compound as such. It is not proposed to continue the investigation any further and this publication is just to point out the existence of this compound.

The experimental work in this investigation was done by one of the authors (G. N. R.), at the Indian Institute of Science, Bangalore. The authors are grateful to Professor M. R. A. Rao of the Chemistry Department of this Institute for providing the material for study.

1. Wyckoff, R. W. G., *Crystal Structures*, Vol. I, Interscience, New York, 1948.

THE GLYCOPROTEIN FRACTIONS IN CEREBRAL TISSUES FROM VARIOUS ANIMALS

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IN one of our previous reports[1] the method for the isolation of glycoproteins from brain tissues has been described. On the basis of the results obtained from the present investigations, besides other studies, a comparison between the levels of the individual glycoprotein fractions in various animals was carried out. These fractions remain in colloidal dispersion in physiological solution and are constant at pH 4·40. In the present report the results obtained have been given.
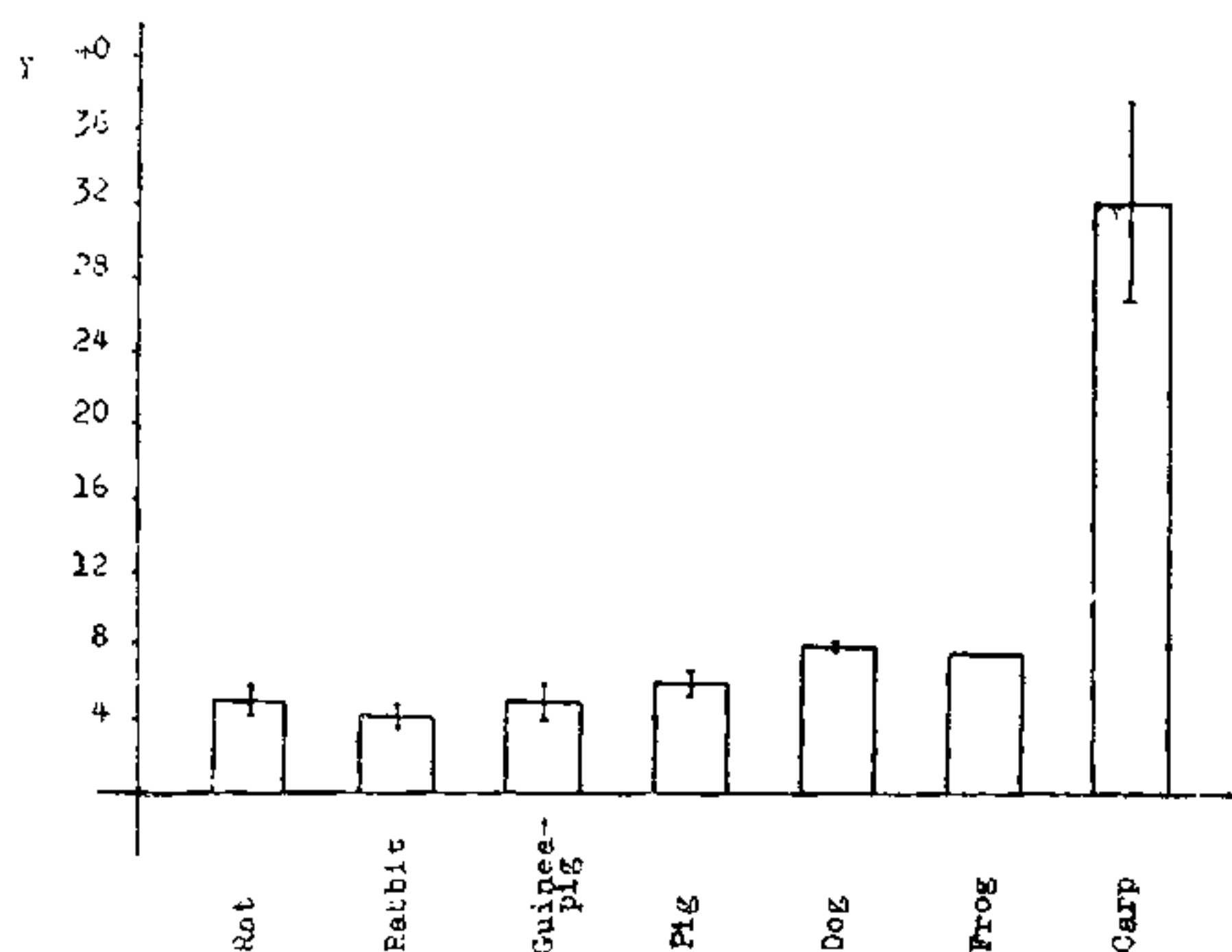

FIG. 1. Protein-bound hexose in brain tissue (Fraction soluble at pH 4·40). Y = mgm.% bound hexose/100 gm. fresh brain tissue.

The experiments were carried out on two types of domestic animals (pig, dog), three kinds of laboratory animals (rat, guinea-pig, rabbit) and on two kinds of cold-blooded animals (frog, carp). The bigger animals were killed by exsanguination from the cervical artery or by means of a heart cannula (pig, dog, rabbit). The freshly autopsied brains were thoroughly washed, stripped of investing meninges and then parts of the hemispheres containing equal amounts of white and grey matter investigated. The little animals (rat, guinea-pig, frog, carp) were killed by decapitation and the whole brains were investigated. In the case of carps and frogs 3, 5 and 11 brains, respectively, had to be combined because the quantity of a single brain specimen was too small.

The homogenized brain tissues were diluted with physiological solution (for 1 gm. tissue 20 ml. physiological solution), centrifuged and the supernatant brought to pH 4·40 ± 0·05 with acetate buffer. At this pH the precipitation of the protective colloids takes place. The material is centrifuged again after which the clear supernatant is obtained in which the total amount of proteins (method by Kjeldahl) and the bound hexose may be determined. The bound hexose was determined by the orcin method which was devised by Stary *et al.*[2] when investigating the cerebrospinal fluids.[3] The determinations were always carried out in duplicate or triplicate. In the preceding paper[1] the procedure and the method have been described in detail.

The results have been summarized in Table I. In the warm-blooded animals and in the frogs the values of bound hexose are on the whole well balanced and range between 4 and 8 mgm./ 100 gm. fresh brain tissue. That means that it forms 0·7 to 1% of the weight of the proteins