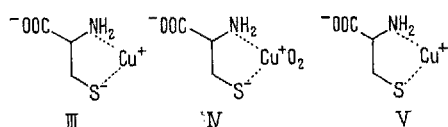
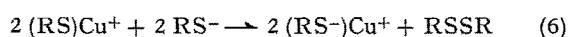
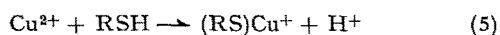
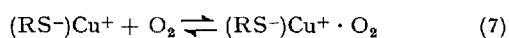


Chelate von der Struktur II<sup>13</sup>, in der wiederum Liganden-  
gruppen  $-N(R)^-$  vorliegen, die für den völlig andersartigen  
Reaktionsverlauf verantwortlich sein dürften.

(c) Cystein (RSH) wird durch  $Cu^{2+}$  über eine Radikal-  
zwischenstufe zu Cystin oxydiert. Bei der Reaktion äqui-  
valenter Mengen entsteht eine violettbraune Partikel,  
der wir die Struktur eines Radikalkomplexes V zuschrei-  
ben (5). Im Überschuss an Cystein findet eine Verdrän-  
gung des Radikalliganden RS durch die stärkere Base  
 $RS^-$  statt, wobei unter Dimerisierung des Radikals  $RS^-$   
Cystin gebildet wird (6). Die Stabilität des farblosen  $Cu^+$ -  
Komplexes III ist von KOLTHOFF zu ca.  $10^{19}$  bestimmt  
worden<sup>14</sup>.



Wird eine farblose Lösung von III mit Luft gespült, so  
entsteht nach kurzer Zeit ein gelbbraunes Addukt IV<sup>15</sup>.  
Die Bildungsreaktion (7) muss reversibel sein, denn Ein-  
leiten von  $N_2$  oder Zugabe von  $CN^-$  bewirkt partielle Ent-  
färbung der Lösung, somit Verschiebung des Gleich-  
gewichts (7) nach links. Addukt IV ist aber sehr unbestän-  
dig und wird nach wenigen Minuten in irreversibler Weise



zum violettbraunen Radikalkomplex V oxydiert. Aber  
auch V ist instabil. Beim längeren Einwirken von  $O_2$

findet unter Entfärbung Oxydation zur  $Cu^{II}$ -Stufe statt,  
und unter Dimerisierung von  $RS^-$  entsteht schliesslich  
Cystin.

In der Reaktionsfolge  $III \longrightarrow IV \longrightarrow V$  ist bemerkens-  
wert, dass spezifische Bindungseffekte in III, durch die  
Ligandengruppe  $RS^-$  hervorgerufen, das Metallion  $Cu^+$   
zur reversiblen Addition von  $O_2$  befähigen. Die Vermu-  
tung, wonach im Hämocyanin das Metall über eine SH-  
Gruppe an das Protein gebunden ist<sup>16</sup>, wird somit durch  
die vorliegenden Resultate bestätigt<sup>17</sup>.

**Summary.** The reactivity of copper(I)-complexes to-  
wards molecular oxygen in relation to some copper con-  
taining enzymes has been studied. The oxydation of  
simple amine-complexes proceeds at a rate of about  
 $10^3$ – $10^4$  Mol<sup>-1</sup>Lt Min<sup>-1</sup>. Replacing the amine by amides  
and peptides has a strong retarding effect. A copper(I)-  
cysteine complex exhibits the interesting property of add-  
ing  $O_2$  reversibly.

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<sup>14</sup> I. M. KOLTHOFF und W. STRICKS, J. Amer. chem. Soc. **73**, 1723 (1951).

<sup>15</sup> Möglicherweise binuklear:  $(RS^-)Cu^+ \cdot O_2 \cdot Cu^+(RS^-)$ .

<sup>16</sup> L. C. G. THOMSON, M. HINES und H. S. MASON, Arch. Biochem. Biophys. **83**, 88 (1959).

<sup>17</sup> Dem Schweizerischen Nationalfonds zur Förderung der wissen-  
schaftlichen Forschung danken wir für einen Forschungskredit.

## PRO EXPERIMENTIS

### The Direct Conversion of Wood Charcoal to Lithium Carbide in the Production of Acetylene for Radiocarbon Dating

Most laboratories engaged in radiocarbon dating use gas  
proportional counters filled with pure carbon dioxide,  
acetylene, or methane. The advantage of acetylene lies in  
the fact that it contains two carbon atoms per gas mole-  
cule and thus introduces twice as much radiocarbon into  
the counter for a given filling pressure. In addition,  
acetylene has good counting characteristics and is less  
sensitive to impurities than carbon dioxide. Moreover,  
the preparation procedure can be arranged so as auto-  
matically to eliminate any radon present in the sample.  
The disadvantage of acetylene arises from the fact that  
the sample preparation takes somewhat longer than it  
does in the case of, for instance, carbon dioxide.

Two completely different methods have so far been  
used for preparing acetylene for radiocarbon dating. The  
one method, of BARKER<sup>1</sup>, involves the combustion of the  
sample to carbon dioxide, the reaction of the carbon  
dioxide with lithium, the conversion of the lithium car-  
bide to acetylene by addition of water, and the purifica-  
tion of the sample by passing it in turn over potassium  
hydroxide solution and phosphoric acid.

The other method, of SUESS<sup>2</sup>, involves the combustion  
of the sample to carbon dioxide, the conversion of the car-

bon dioxide to strontium carbonate, the reduction of the  
strontium carbonate to strontium carbide with excess  
magnesium, the conversion of the strontium carbide to  
acetylene, and the purification of the sample by passing  
it over cooled charcoal.

It is obvious that any method of shortening the sample  
preparation would make acetylene a much more attrac-  
tive proposition as a counting gas for radiocarbon dating.  
With this end in view we have successfully developed a  
new method of preparing acetylene from wood charcoal.

Laboratories engaged largely on archaeological work,  
such as our own, deal predominantly with charcoal  
samples and there appears to be no reason why such sam-  
ples should not be reacted directly with lithium to form  
lithium carbide, thus avoiding the necessity for the initial  
combustion.

It has long been known that graphite will react directly  
with lithium, to form lithium carbide, at red heat<sup>3</sup>. We  
have accordingly reacted samples of dry wood charcoal,  
as supplied to us by archaeologists and pretreated in the  
usual manner, containing 6 g of carbon with excess li-  
thium ( $14\frac{1}{2}$  g) by heating under vacuum at about 800°C  
in a steel furnace. Some gas is evolved during the reaction

<sup>1</sup> H. BARKER, Nature **172**, 631 (1953).

<sup>2</sup> H. E. SUESS, Science **120**, 5 (1954).

<sup>3</sup> J. W. MELLOR, *A Comprehensive Treatise of Inorganic Chemistry and Theoretical Chemistry* (1956), vol. V, p. 847.

and the reaction vessel is evacuated continuously in the initial stages of the reaction by means of a rotary pump. Towards the end of the reaction, a diffusion pump is coupled to the system as well. Completion of the reaction is accompanied by a marked improvement in the vacuum obtainable.

The period of heating required appears to depend on the precise nature of the charcoal and varies from 1 to 2 h. No advantage seems to be gained by crushing the charcoal, and large pieces appear to react just as rapidly as a coarse powder.

Further treatment of the sample was identical to that used by BARKER and conversion was found to be better than 95%, thus eliminating any possibility of fractionation. As an additional check on the method, the count of a randomly chosen sample was compared with that of an identical sample prepared by the BARKER method and found to be  $13.54 \pm 0.06$  as opposed to  $13.64 \pm 0.07$ . Using this new method it is possible to get a sample of pure dry acetylene into the counter in less than 5 h. Since the apparatus is essentially the same as that used by

BARKER, samples other than charcoal, such as wood, shell, or bone, as well as the N.B.S. oxalic acid standard, can still be prepared without any inconvenience by the method of BARKER<sup>4</sup>.

**Résumé.** On décrit ici une nouvelle méthode pour convertir, dans un four d'acier à 800°C, le charbon de bois directement en carbure de lithium produisant de l'acétylène pour déterminer le carbone radioactif. La méthode offre une notable économie de temps pour la préparation des échantillons et le produit de conversion atteint le 95% ou davantage.

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<sup>4</sup> I would like to acknowledge the help of Miss E. A. HEGGARTY, who has carried out most of the work of preparing and counting the samples.

## Crystalline

### $\beta$ -D-Ribofuranosyl- $\beta$ -D-ribofuranoside: A New Diriboside Synthesis

ZAMENHOF et al.<sup>1</sup> have proposed that the type specific substance of *Hemophilus influenzae* b is a polyribophosphate polymer whose ribose units are present as disaccharides with the structure  $\beta$ -D-ribofuranosyl- $\beta$ -D-ribofuranoside (III). While a chemical synthesis<sup>2</sup> of this substance *via* a Koenigs-Knorr reaction gave a well characterized hexabenzooate derivative II, hydrolysis provided the free sugar only as a non-crystalline substance.

In connection with another project in these laboratories, it was of interest to learn whether 1-*o*-acetyl 2,3,5-tri-benzoylribofuranoside (I)<sup>3</sup>, when treated in benzene with boron trifluoride etherate could yield any C<sub>1</sub>-phenylated ribose<sup>4</sup>.

While none of this substance was isolated, a new crystalline product, m.p. 143–144°,  $[\alpha]_D + 35.2^\circ$ ,  $C = 0.475$  (chloroform) could be obtained<sup>5</sup>. Analysis and further investigation suggested that this substance was identical with the hexabenzooate II and comparison with the reported physical constants upheld this view<sup>6</sup>.

Hydrolysis of II was effected with fresh sodium methoxide in anhydrous methanol. Following evaporation, the residue was dissolved in water and percolated through Dowex-50-pyridinium salt to yield III, crystallized from absolute ethanol m.p. 158–160°,  $[\alpha]_D - 102^\circ$ ,  $C = 0.47$  (water),  $C_{10}H_{18}O_9$ . Found: C, 42.74; H, 6.38; O, 50.71. Direct comparison of this crystalline substance with the amorphous natural product<sup>1</sup> by means of paper chromatography showed identical mobilities<sup>7</sup>.

Examination of the n.m.r. spectra of II and III has allowed an unambiguous decision in favour of the  $\beta, \beta'$ -configuration previously suggested<sup>2</sup> on the basis of rotational data. In deuterium oxide for III and deuteriochloroform for II, the anomeric protons appear in sharp singlets,  $\delta$  5.68 for III and  $\delta$  5.73 for II<sup>8</sup>, thereby demonstrating that the coupling constants with the adjacent protons on C<sub>2</sub> and C<sub>2'</sub> have the value  $J = 0$ . Reference to the Karplus equation and modification thereof<sup>9</sup> indicates that coupling constants with  $J$  values equal to 0 occur only when the

angle between the protons in question is in the neighborhood of 90°. Since molecular models of II and III show that such angles may be achieved only when the anomeric protons are in the  $\alpha$ -configuration (i.e. trans to those at C<sub>2</sub> and C<sub>2'</sub>), it follows that the sugars must be joined by  $\beta, \beta'$  linkages<sup>10</sup>.

**Zusammenfassung.** Behandlung von 1-*o*-Acetyl-2,3,5-tri-*o*-benzoyl- $\beta$ -D-ribofuranosid mit Bortrifluorid-ätherat gibt ein Diribosid-hexabenzooat, welches zu reinem, kristallinem  $\beta$ -D-Ribofuranosyl- $\beta$ -D-ribofuranosid hydrolysiert werden kann.

J. A. ZDERIC<sup>11</sup>

*Syntex Institute for Molecular Biology, Palo Alto (California, U.S.A.), July 25, 1963.*

<sup>1</sup> E. ROSENBERG and S. ZAMENHOF, *J. biol. Chem.* **236**, 2845 (1961) and references therein.

<sup>2</sup> E. ROSENBERG and S. ZAMENHOF, *J. biol. Chem.* **237**, 1040 (1962).

<sup>3</sup> E. F. RECONDO and H. RINDERKNECHT, *Helv. chim. Acta* **42**, 1171 (1959).

<sup>4</sup> Friedel-Crafts alkylations employing sugar halides and anomeric acetates have been reported. See, W. A. BONNER, *Advanc. carbohyd. Chem.* **6**, 251 (1951).

<sup>5</sup> Later, it was shown that the use of methylene chloride instead of benzene provided more reproducible yields.

<sup>6</sup> For a mineral acid catalyzed dipentose synthesis employing trimethylxofuranose, see H. G. BORTS, E. L. HIRST, and J. A. B. SMITH, *J. chem. Soc.* **1930**, 658.

<sup>7</sup> We are grateful to Dr. ZAMENHOF for advising us of his results prior to publication and for making the direct comparison reported in solvent systems A and C (see ref. <sup>1</sup>).

<sup>8</sup> The spectra were recorded on a Varian A-60 spectrometer. Tetramethylsilane was used as a standard externally for III and internally for II.

<sup>9</sup> M. KARPLUS, *J. chem. Phys.* **30**, 11 (1959). – R. J. ABRAHAM, L. D. HALL, L. HOUGH, and K. A. McLANGLAN, *J. chem. Soc.* **1962**, 3899.

<sup>10</sup> The author is indebted to Dr. A. WALSER for discussions regarding the n.m.r. spectra.

<sup>11</sup> On leave at the Eidg. Technische Hochschule, Zürich (Switzerland).