

which sufficient ammonium hydroxide is added to give a decided odor. The crystals are washed with ether. When dry the purification is completed by a recrystallization from hot benzene; yield, 2 g.; white microscopic needles. The compound shows a slight shrinkage at about 139° and melts at 142-143°. It is tasteless and odorless. Concentrated sulfuric acid gives a colorless solution which upon heating becomes a faint straw color.

Anal. Calcd. for $C_9H_{12}O_2N_2$: C, 60.0; H, 6.66; N, 15.56. Found: C, 60.10; H, 6.72; N, 15.64.

The compound is soluble in hot water, ethanol, amyl alcohol and hot benzene. It is very slightly soluble in ether.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF ARKANSAS
FAYETTEVILLE, ARKANSAS
RECEIVED AUGUST 23, 1930
PUBLISHED OCTOBER 6, 1930

E. WERTHEIM

COMMUNICATIONS TO THE EDITOR

DR. C. S. HUDSON'S VIEWS ON THE RELATIONSHIP OF STRUCTURE TO THE OPTICAL ROTATIONS OF SUGARS

Sir:

Dr. C. S. Hudson has not utilized the means which were open to him to test the validity of his views by direct chemical experiments. The basis on which he develops his argument is the presumed existence, which his statistical methods enable him to detect, of a new form of mannose (calculated $[\alpha]_D + 77^\circ$) in derivatives of 4-glucosido-mannose, obtainable from cellobiose through cellobial. If this foundation for his scheme fails, then the entire superstructure of rival formulas which he has raised upon it must collapse.

A survey of his two recent papers [THIS JOURNAL, 52, 1680, 1707 (1930)] has led me to select for this critical test an experimental method which he has tacitly approved: he has accepted and utilized the observation of Fischer and Armstrong that β -methylmaltoside gives rise by enzyme hydrolysis to β -methylglucoside without ring change. Implicit in Dr. Hudson's scheme, therefore, is the expectation that 4-glucosido- α -methylmannoside will yield by enzyme cleavage his hypothetical α -methylmannoside ($[\alpha]_D + 125^\circ$), inasmuch as this is the glycoside of the unknown form of mannose to which he has assigned the 1,5-ring.

With my colleague Dr. E. L. Hirst and other co-workers (R. J. W. Reynolds, H. R. L. Streight, H. A. Thomas, J. I. Webb and Miss M. Plant) I have prepared and investigated the chemical behavior of both 4-glucosido- α -methylmannoside and 4-galactosido- α -methylmannoside to which the 1,4-ring cannot apply since the 4-position in the mannose residue is occupied by the biose link. Both these substances are hydrolyzed by

emulsin and yield the ordinary known form of α -methylmannoside ($[\alpha]_D +79^\circ$) which is the pyranoside (1,5-ring).

The above biosides are prepared in the same way as the bioses, namely, from cellobial and lactal by the action of perbenzoic acid, but in the presence of methyl alcohol instead of water. The same 4-glucosido- α -methylmannoside has also been obtained from acetobromo-glucosidomannose.

Had Dr. Hudson tried these experiments it is difficult to see how he could have committed himself to speculations that are at variance with this and with much more chemical evidence which is on record. Moreover, the rotations of these biosides and of the corresponding bioses are widely divergent from those required by his system of classification based on epimeric differences with cellobiosides and lactosides and the free sugars. The "principle of optical superposition" cannot be applied uniformly throughout the sugar group. The results now summarized are in complete agreement with the sugar formulas we have established by methylation studies, lactone formation and degradation, and by a comparison of the reaction velocities of glycosides under hydrolysis, and by other direct chemical methods.

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RECEIVED JULY 30, 1930
PUBLISHED OCTOBER 6, 1930

POSSIBLE USE OF THE POULSEN ARC AS A MEANS OF DETECTING TRACES OF IMPURITIES IN METALS

Sir:

It has been shown by one of us in conjunction with E. Z. Stowell¹ that an atmosphere of hydrogen and usually cathode materials which are elements of even atomic number are necessary to produce radio frequency oscillations in the Poulsen Arc.

In the non-oscillating or ordinary direct current arc in hydrogen, the spectra of copper and sodium were revealed when these elements were used as cathodes. Upon connecting the oscillating circuit, the spectra of copper or sodium were either entirely suppressed, or appeared only faintly. Simultaneously the spectra of elements such as zinc, titanium and aluminum which will support oscillation, and which were present in small amount as impurities in the cathode metal, either appeared or if previously present were greatly accentuated.

The spectrum of H_B showed the presence of more atomic hydrogen in the oscillating than in the non-oscillating arc. Chemical analysis of the electrolytic copper showed titanium and aluminum present as 0.005 and 0.0045%, respectively.

¹ Stowell and Redeker, *Phys. Rev.*, **34**, 978 (1929).