

chloride and the esters produces oily or waxy residues.

4. The reaction of selenium tetrachloride on the esters of salicylic acid goes through several

stages. It seems probable that a number of other compounds might be isolated if proper conditions can be found.

LAFAYETTE, INDIANA

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[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Structure of Sedoheptulosan (Anhydro-sedoheptose)¹

By C. S. HUDSON

In the present article it will be shown that there is at hand, from the published work of several investigators, conclusive experimental evidence that sedoheptulosan,² the remarkable anhydride that is spontaneously formed from sedoheptulose in acid solution, is not related in structure to levoglucosan, as generally supposed, but contains a septanose ring and an ethylene oxide ring. This result necessitates a modification of present views regarding the stability of ring systems in carbohydrates that have the configuration which pertains in common to sedoheptulose and altrose; it may have further consequences as regards other sugars because of the new structures that it discloses.

The argument requires for clearness a presentation that follows the historical order.

At the time of the discovery of sedoheptulose² in *Sedum spectabile*, the sugar (a ketose) was reduced by sodium amalgam to yield two heptitols which were named provisionally α - and β -sedoheptitol, and it was made probable that α -sedoheptitol is identical with volemitol, a heptitol of unknown configuration, which Bourquelot³ had isolated from the mushroom, *Lactarius volemus*; the identity was later established by direct comparison of the two substances,⁴ and by a thorough study of the derivatives of volemitol.⁵ Investigation of the configuration of sedoheptulose was then undertaken by La Forge,⁶ who advanced in 1920 the view that it must be either (I) or (II) or a mirror image of one of these.

(1) Publication authorized by the Surgeon General, United States Public Health Service.

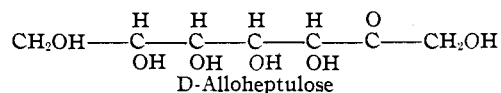
(2) La Forge and Hudson, *J. Biol. Chem.*, **30**, 61 (1917). This name seems preferable to the original designation, *anhydro-sedoheptose*, and likewise *sedoheptulose* to *sedoheptose*.

(3) Bourquelot, *Bull. soc. mycologique de France*, **5**, 132-163 (1889). This volume is in the library of the U. S. Dept. of Agriculture, Washington, D. C.

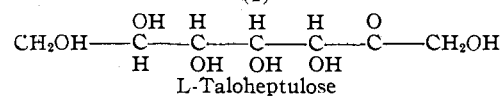
(4) La Forge, *J. Biol. Chem.*, **43**, 375 (1920); La Forge and Hudson, *ibid.*, **79**, 1 (1928).

(5) Ettel, *Coll. Czechoslovak Chem. Comm.*, **1**, 288 (1929).

(6) La Forge, *J. Biol. Chem.*, **42**, 367 (1920).

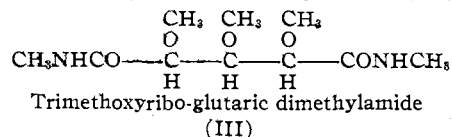


(I)



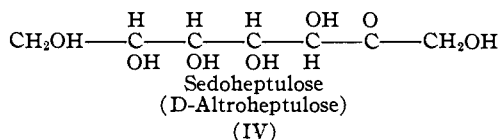
(II)

It is clear today that a mistake was made by La Forge in this allocation of configuration; it was corrected by Ettel in 1932 (*vide infra*) but in the meantime it had adversely affected the reasoning in a brilliant experimental investigation by Hibbert and Anderson,⁷ next to be described. In 1930 these workers undertook the determination of the positions of the two rings in sedoheptulosan by methylation methods, basing the study naturally upon La Forge's configurational allocations (I) or (II). The fully methylated derivative proved to be a crystalline substance, tetramethyl-sedoheptulosan; its oxidation by strong nitric acid yielded a trimethoxyglutaric acid which was isolated as a crystalline dimethylamide (m. p. 145-146°, no rotation, correct analysis for C, H, N and OCH₃). Only four trimethoxyglutaric acids are possible, namely, those derivable ultimately from the four pentoses (counting the D- and L- forms of tri-methoxy-arabinoglutaric acid as two acids), and only two of these can be optically inactive, namely, the xylo- and ribo-forms; trimethoxyxylo-glutaric dimethylamide had been well studied⁸ (m. p. 167-168°) and Hibbert and Anderson concluded that their substance, of much lower melting point, must be the hitherto unknown trimethoxyribo-glutaric dimethylamide (III).

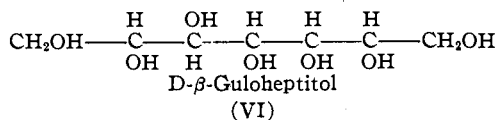
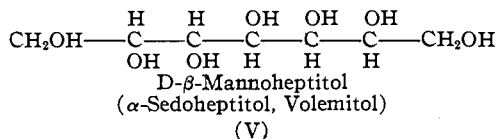


(7) Hibbert and Anderson, *Canadian J. Research*, **3**, 306 (1930).

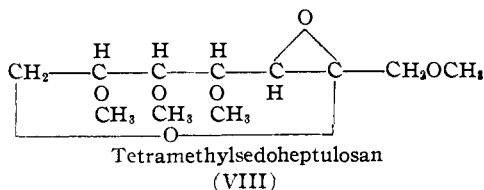
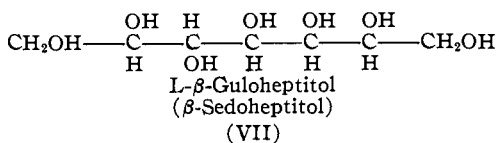
(8) Haworth and Jones, *J. Chem. Soc.*, 2352 (1927).



The inferences which Hibbert and Anderson then drew regarding the positions of the two rings in sedoheptulosan may be passed over, as they depend upon the incorrect formulas of La Forge (I) and (II) and are not pertinent to the present argument. It may suffice to say that they considered the structure of sedoheptulosan to be similar to that of levoglucosan. In 1932 Ettel⁹ changed the aspect of the whole matter by proving that the true configuration of sedoheptulose is (IV); he accomplished this by establishing the identity of α -sedoheptitol and volemitol with the known¹⁰ D- β -mannoheptitol (V) and by showing



that β -sedoheptitol is the enantiomorph of the known¹¹ D- β -guloheptitol (VI) and therefore has the formula (VII).



Lastly, in 1936 Levene and Compton¹² had occasion in a research that was not concerned with sedoheptulose to prepare from 2,3,4-trimethyl-*d*-ribose the di-methylamide of trimethoxyribo-glutaric acid; they found the substance to show no rotation and to melt at 145–146°, exactly as reported by Hibbert and Anderson (*vide supra*).

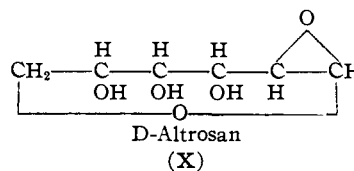
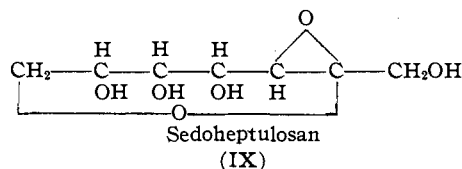
(9) Ettel, *Coll. Czechoslovak Chem. Comm.*, **4**, 504, 513 (1932).

(10) Peirce, *J. Biol. Chem.*, **23**, 327 (1915); La Forge, *ibid.*, **28**, 521 (1917).

(11) La Forge, *ibid.*, **41**, 251 (1920).

(12) Levene and Compton, *ibid.*, **116**, 184 (1936).

The data that have thus been supplied by the researches of Hibbert and Anderson, of Ettel, and of Levene and Compton seem completely trustworthy; they lead unequivocally to the conclusion that will now be drawn. Assuming the correctness of (IV) for the configuration of sedoheptulose (from Ettel's work) and of the observation that tetramethylsedoheptulosan yields by oxidation trimethoxyribo-glutaric acid (from the work of Hibbert and Anderson and of Levene and Compton) there is only one stereo-structure that can apply to tetramethylsedoheptulosan, namely, (VIII), and there follows for sedoheptulosan necessarily the stereostructure (IX). This is an unusual structure (an ethylene



oxide ring and a septanoid ring with no pyranoid or furanoid ring) but the clearly established experimental facts permit no other interpretation. There are three additional facts which conform to this formula. (1) When Hibbert and Anderson⁷ let one mol of sedoheptulosan react with two mols of trityl chloride only a mono-trityl derivative could be isolated, showing that sedoheptulosan carries only one primary hydroxyl group. (2) Richtmyer and Hudson¹³ found that *d*-altrose, the configuration of which is analogous to that of sedoheptulose, establishes in acid solution an equilibrium between a copper reducing form and a non-reducing modification, a behavior quite like that of sedoheptulose; this unusual anhydride formation thus appears to be characteristic of the altrose configuration. It is apparently caused by the easily opened ethylene oxide ring in the septanose. (3) The fact that the numerous studies of arabinose and its derivatives have never disclosed any such anhydride formation, though arabinose is like altrose in the configuration of its three asymmetric carbon atoms, is readily understood if one of the rings in the anhydrides is septanoid, since a pentose cannot form such a

(13) Richtmyer and Hudson, *THIS JOURNAL*, **57**, 1716 (1935).

ring. It seems probable that the structure of the anhydro-form that *d*-altrose generates in acid solution is analogous to that of sedoheptulosan and may be written as (X), the substance being a D-altrosan.¹⁴

It is not possible on present evidence to decide whether either the ethylene oxide or the septanoid ring is present in the reducing form of sedoheptulose or of altrose. The pyranoid or furanoid ring is not excluded in the reducing structure, but it is certainly questionable whether crystalline *d*-altrose, of $[\alpha]_D +33^\circ$, with no mutarotation, is of either the pyranose type or the furanose. Altrose and sedoheptulose are different in behavior in certain fundamental aspects from the sugars that have given rise to most of our generalizations in sugar chemistry. Various extensions of these views to give speculative explanations of some of

(14) It is emphasized that at the present time the formula (X) for D-altrosan rests solely upon the apparent analogy to sedoheptulosan (IX). The article by Robertson and Griffith (*J. Chem. Soc.*, 1193 (1935)), furnishes observations in the altrose series which seem difficult to interpret on the basis of (X), but I hope that the questions may soon be answered through additional experimental data.

the anomalies that have been observed with certain of the sugars, the lack of mutarotation in some reducing sugars and its complex character in some others, the agreement of rotations with the isorotation rules in some cases and a failure in others, are obviously possible, but it is too early now to discuss them. New experimental data must first be obtained. Possibly such anhydride formation may be found to occur with sugars of configurations different from that of altrose.

Summary

It is shown that sedoheptulosan possesses an unusual structure, one of its rings being an ethylene oxide form and the other a septanoid ring. This result is extended by analogy to the anhydro-form of altrose. Our present generalizations regarding the ring structures of sugars do not apply to sedoheptulose and altrose; their behavior is exceptional and appears to be due to their tendency to form types of rings that play little or no role in the case of the more common sugars.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Photolysis of the Aliphatic Aldehydes. VI. Acetaldehyde

BY FRANCIS E. BLACET AND DAVID VOLMAN

The discussion of the photochemistry of the aldehydes by Rollefson¹ and Burton² has served to emphasize the fact that additional experimental data, especially in regard to decomposition products, must be obtained before the mechanism of decomposition of these compounds can be fully appreciated. The experimental results reported in this paper appear to settle certain of the questions which have been raised concerning the gaseous decomposition products of acetaldehyde. In addition, other information has been obtained which must be considered in the study of this reaction mechanism.

Experimental Method

The aldehyde was studied in the vapor phase in an apparatus essentially the same as that previously described³ with the exception that since the object of the study was to determine the nature of the gaseous decomposition products, no provision was made to measure quantum yields. The source of radiation was a high pressure mercury arc used in conjunction with a crystal quartz monochromator.

In order to vary the reaction temperature the silica reaction cell was submerged in a water thermostat. The cell was recessed from the wall of the thermostat with the aid of a metal tube of the same diameter. This tube was soldered to the inner wall of the thermostat and connected to the reaction cell by means of a rubber sleeve. Monochromatic light entered the system through a slit placed at the outer end of the metal tube. In experiments carried out below room temperature moisture was prevented from condensing on the front window of the cell by having a drawn-out glass tube carrying a slow stream of nitrogen enter one end of the slit.

After irradiation, the excess acetaldehyde was liquefied by means of a carbon dioxide-alcohol refrigerant and the non-condensable gas removed by means of a Toepler pump. In order to avoid the possibility of differential absorption of the gas by the liquid aldehyde, the condensation trap was warmed and cooled several times with additional pumping carried out after each cooling operation. Some liquid aldehyde collected in the gas holder of the analytical apparatus but this was removed by the introduction of successive potassium hydroxide beads in the sample. The micro methods of analysis which were used have been described elsewhere.⁴⁻⁷

(1) Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

(2) Burton, *ibid.*, **41**, 322 (1937).

(3) Leighton and Blacet, *This Journal*, **54**, 3165 (1932).

(4) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931).

(5) Blacet, MacDonal and Leighton, *ibid.*, **5**, 272 (1933).

(6) Blacet and MacDonal, *ibid.*, **6**, 334 (1934).

(7) Blacet and Volman, *ibid.*, **9**, 44 (1937).