

TABLE I
FILMS OF POLYMERS OF ω -HYDROXYDECANOIC ACID ON WATER

Mean values at temperatures from 21.5 to 26.0°. Concentration of hydrogen chloride in the water 0.01 *M*
Columns 2 and 3 are taken mostly from the paper of Carothers and Van Natta

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Mol. wt.	Density d_{25}^4	Length of molecule in Å.	Vol. of molecule in cu. Å.	Area per molecule at a film pressure			Maximum force f_m	$t =$ thickness of film at a film pressure			$d =$ width of molecular space at			$f \times d$ molecular cross sect. at 3 dynes in sq. Å.	Compressibility of $f=0$
				$f=0$	$f=3$	$f=\text{max.}$		$f=0$	$f=3.0$	$f=\text{max.}$	$f=0$	$f=3.0$	$f=\text{max.}$		
780	1.0957	60	1170	330	290	246	5.7	3.6	4.0	4.8	5.5	4.8	4.1	19.5	0.040
1715	1.0935	133	2590	700	604	556	4.5	3.7	4.3	4.7	5.3	4.5	4.2	19.4	.046
3190	1.0877	248	4840	1260	1080	970	4.2	3.9	4.5	5.0	5.1	4.4	3.9	19.6	.048
4170	1.0814	324	6360	1490	1300	1130	4.5	4.3	4.9	5.6	4.6	4.0	3.5	19.6	.043
5670	1.0751	440	8700	2050	1800	1688	4.4	4.2	4.8	5.2	4.7	4.1	3.8	19.7	.041
7330	1.0715	570	11330	2670	2277	2180	3.8	4.2	5.0	5.2	4.7	4.0	3.8	19.9	.049
9330	1.0668	730	14450	3800	3200	3000	4.0	3.8	4.5	4.8	5.2	4.4	4.1	19.8	.053
16900	1.0627	1320	26200	6440	5510	5270	3.4	4.1	4.8	5.0	4.9	4.2	4.0	19.9	.048
25200	1.0621	1970	39100	10430	8800	8700	3.2	3.8	4.4	4.5	5.3	4.5	4.4	19.9	.052

These relations, particularly 1, 2, 3, 4, 5 and 10, show conclusively that the molecules of these polymers lie flat on the surface. The molecules are anchored in this position by the polar groups at the ends and at every tenth carbon atom. Thus the molecule acts as a type of centipede, with as many as 149 regions of attachment.

The general relations are exhibited by Table I and Figs. 1, 2 and 3.

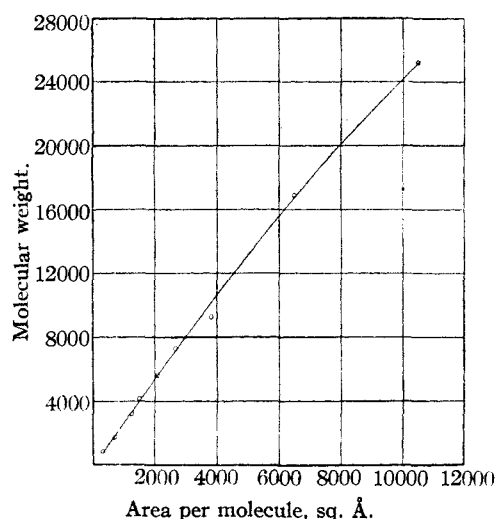


Fig. 3.—Surface area as a nearly linear function of the molecular weight.

The work given here was begun in this Laboratory by Dr. E. H. Fischer.

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RECEIVED MARCH 4, 1935

***d*-GULO-METHYLOSE (6-DESOXY-*d*-GULOSE) AND ITS RELATION TO A REPORTED INVERSION PRODUCT OF *l*-RHAMNOSE**

Sir:

We wish to report the synthesis of a new methyl pentose, *d*-gulo-methyl-ose (6-desoxy-*d*-gulo-ose) by use of the cyanhydrin reaction on *d*-xylo-methyl-ose (5-desoxy-*d*-xylose) [Levene and Compton, *Science*, **81**, 156 (1935)], followed by reduction of the lactone with Na-Hg amalgam in the usual manner. The physical constants of this substance along with several derivatives are recorded below.

Substance	M. p., °C.	$[\alpha]_D$	Solvent
(1) <i>d</i> -Gulo-methyl-ose	Glassy solid	-35.7° (constant)	water
a (substance of Muskat)	amorphous solid ca. 65	+14° → -14°	water
(2) <i>p</i> -Bromophenyl-hydrazone of (1)	135	-16.1° → +9.2°	ethanol
a (substance of Muskat [1a])	162	-6.1° → +13°	ethanol
(3) <i>p</i> -Bromophenyl-osazone of (1)	195-196	±0.00° → 15.3°	pyridine-ethanol 3:2
(4) <i>d</i> -Gulo-methyl-onic lactone	180-181	-68.0°	water
(5) <i>p</i> -Bromophenyl-hydrazide of (4)	132-133	+8.83°	water
(6) <i>d</i> -Gulo-methylonic acid	—	-5.00°	water
(7) Sodium salt of (6)	—	+11.03°	water

The synthesis was undertaken for the purpose of testing the claim of Dr. I. E. Muskat [THIS JOURNAL, **56**, 2653 (1934) (this article, although published as a contribution from the Laboratories of the Rockefeller Institute for Medical Research, was never seen prior to publication by the senior author of this Communication)] that a Walden inversion occurred during the alkaline hydrolysis

of 5-*p*-toluenesulfonyl-2,3-acetone methylrhamno-furanoside. A comparison of the properties of the free sugar and its derivatives prepared by Muskat with those of the newer substances reported above shows clearly that the product obtained by this author is not *d*-gulo-methylose.

It may be added that Dr. A. L. Raymond of this Laboratory has failed to observe a Walden inversion in the cases of 3-*p*-toluenesulfonyl diacetone glucose and 3-*p*-toluenesulfonyl-5-methyl monoacetone xylose.

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P. A. LEVENE
JACK COMPTON

RECEIVED MARCH 11, 1935

6-DESOXY-*d*-GULOSE*

Sir:

In the preceding note P. A. Levene and Jack Compton [THIS JOURNAL, 57, 777 (1935)] present some data on a supposed 6-desoxy-*d*-gulose which they have prepared. The properties of this substance seem to differ from an inverted compound previously obtained by this author.

While at the Rockefeller Institute as a National Research Council fellow, I studied, independently, the mechanism of Walden inversion of sugars. As a result of theoretical considerations it was decided to investigate the alkaline hydrolysis of two *p*-toluenesulfonyl esters of rhamnose. It was definitely established that an inversion occurred during the hydrolysis of both sugars. No effort was made to determine the structure of the inverted product, for neither of the sugars nor derivatives isolated in this work had been previously prepared. Insufficient material was available to determine the structures by other than empirical and, therefore, unreliable means. The inverted sugar obtained from the rhamnofuranoside was assumed to be 6-desoxy-*d*-gulose since it was not clear how any other product could be formed under the particular conditions of the experiment. I may mention here that in the original paper as sent to the Journal this fact was clearly stated, but due to the necessity of limiting its size, it was inadvertently omitted in the final paper. Consequently, it is true that the author did not definitely establish the identity of the inverted product as 6-desoxy-*d*-gulose.

An examination of the evidence presented by Levene and Compton for the structure of their

* This letter was received prior to the addition of items six and seven to the table in the preceding communication—EDITOR.

product reveals the following facts. Their starting material, 5-desoxy-*d*-xylose, is a sirup. This was treated with hydrogen cyanide, hydrolyzed to a lactone, and then reduced to the aldose sugar. It may be well to point out that two different sugars, each having two forms (furanose and pyranose) may result from such reactions. In other words, any or all of four different compounds may have composed the final product. Levene and Compton must have overlooked this simple fact, since they present no evidence that the sugar they have obtained is a 6-desoxy-*d*-gulose. Of course the rotations of the lactone and of its bromophenylhydrazide may be taken as indications of such a structure, but insufficient work has been done on these particular sugars to use such empirical rules as anything but supporting data. Consequently, Levene and Compton do not know the structure of their sugar and their criticism is therefore invalid. From the data they present it may be that they have an entirely different sugar or simply an impure form of 6-desoxy-*d*-gulose.

Levene and Compton state that "A. L. Raymond of this Laboratory has failed to observe a Walden inversion in the cases of 3-*p*-toluenesulfonyl diacetone glucose and 3-*p*-toluenesulfonyl-5-methyl-monoacetone xylose." The author wishes to call their attention to page 2653 of his article in which it is stated "It is not suggested that a Walden inversion will necessarily occur in all reactions of type (II)," and on page 2654, "Whether an inversion will or will not occur, and if it will, to what extent, will depend on the steric effects in the sugar molecule and the experimental conditions." It may be that no inversion has occurred in these two sugars or, as Levene and Compton so aptly put it, "Raymond has failed to observe it."

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IRVING E. MUSKAT

RECEIVED MARCH 21, 1935

THE ALLEGED ISOTOPIC INTERCHANGE BETWEEN WATER AND ACETYLENE

Sir:

It has recently been reported [L. H. Reyerson and S. Yuster, THIS JOURNAL, 56, 1426 (1934)] that an isotopic interchange takes place between water and acetylene in alkaline solution. Experiments in this Laboratory have failed to give any in-