[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

FLUORO-ACETYL DERIVATIVES OF SUGARS. II. OPTICAL ROTATION AND ATOMIC DIMENSION

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Introduction

Since the well-known discovery by Le Bel and van't Hoff of the coincidence of the presence of an asymmetric carbon atom in the molecule and the action of the latter on the plane of polarized light, organic and physical chemists have diligently studied this phenomenon.[1] This marked interest has undoubtedly been inspired by the hope that this relation, coupled with ability to synthesize organic compounds of desired structure, would permit a further insight into the subject.

It is noteworthy that in proportion to the efforts made, the results are rather small. Van't Hoff's principle of optical superposition has given interesting results in the hands of Hudson[2a] and Levene.[2b] The application of this principle and other related rules established by these authors are especially useful for determining the structure of organic compounds containing asymmetric carbon atoms. Nevertheless, the isolated and uncorrelated position of the property of optical rotation among other physical constants was not changed by these and numerous other investigations in which the influence of concentration of the solute, temperature, nature of the solvent and (most successfully) the wave length of the light (dispersion) were studied.[3] It has been pointed out[4] that the theory of Drude forms the basis for arranging and combining the facts regarding rotatory dispersion. A theory by Livens[5] based on a general theory by H. A. Lorentz, establishing a relation between the optical rotation and the refractive index, is also regarded as promising for development. Inasmuch, however, as these theories have a purely physical basis without introducing a chemical viewpoint, it would appear that they are not capable of yielding a workable method for experimental treatment of the subject in its general form.[6] This objection does not, however, hold for the

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[1] For a discussion of the general rule for asymmetry and the limitations of the asymmetry of the molecule denoted by "asymmetric carbon atom," see Jaeger, *Bull. soc. chim.*, **33,** 853 (1923).

[2] (a) Hudson, THIS JOURNAL, **31,** 66 (1909); **35,** 1566 (1916); **39,** 462 (1917); **40,** 813 (1918). (b) Levene, *Biochem. Z.*, **124,** 42 (1921).

[3] For literature see Stewart, "Stereochemistry," Longmans Green and Co., London, 2nd ed., **1919,** p. 86.

[4] "Annual Reports on the Progress of Chemistry," London, **1914,** p. 14.

[5] Ref. 3, p. 90.

[6] See also Experim. Prüf. einiger Theorien des natürl. Drehungsvermögens opt. aktiver Lösungen, by Paul Wetterfors, *Z. Physik*, **8,** 229 (1922).

theory of Guye (at least in its restricted form) which is an attempt to correlate the rotation and the difference in weight of the 4 asymmetric groups, without taking into account the distance of these groups from the center of gravity of the molecule. In its restricted form, the theory of Guye has been extensively tested by many organic chemists, the results disproving the validity of the theory.[7]

Theoretical Discussion

Notwithstanding these results, it seemed worth while to continue the search for some relation between the optical rotation and the weights of the asymmetric groups. Whereas former investigators changed an asymmetric group to a next higher one of the same homologous series and compared the rotations of the resulting derivatives, it appeared simpler to compare the rotations of derivatives which differ *only* in having an asymmetric halogen replaced by another halogen. With this type of derivatives the influence of the length of the chain may be eliminated. Furthermore, it is an important fact that the affinity of the halogens for hydrogen and oxygen changes regularly when they are compared successively according to their position in Mendeleieff's table; in addition to the *direct* union of the halogen with the carbon atom, secondary bonds to hydrogen and oxygen must also be taken into account. Since the influence of these affinities varies gradually and in a regular manner in the halogen series and only single atoms are considered, we may suppose that the *position* which the halogen occupies in the molecule is not changed when one halogen is replaced by another. Indeed, by comparing the optical rotations of chloro-, bromo- and iodo-tetra-acetylglucose, it was found that the increase in rotation is proportional to the increase in atomic weight. The data are compared in Table II, together with those for the analogous cellose derivatives. The fundamental thought of Guye, that the difference in weight of the asymmetric groups determines the rotation, so far as these data are concerned, is therefore supported by a comparison between the atomic weights and *molecular* rotations. It is evident, however, that a better agreement is obtained in the case of the *specific* rotations. It seemed worth while to extend this relation by preparing the analogous fluorine derivatives and including their values in the comparison. The preparation of the fluoro-acetyl derivatives of glucose, xylose and cellose and the determination of their specific rotations have been described by the author.[8] Of the other fluoro-acetyl derivatives of sugars, which have been subsequently prepared, fluorotetra-acetyl*fructose* will also be considered in this relation, inasmuch as the author has succeeded in preparing the corresponding *bromo*tetra-acetylfructose in crystalline condition

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[7] H. Landolt, "Das optische Drehungsvermögen organischer Substanzen," Vieweg, Braunschweig, 2nd ed., **1898**, p. 268. Also Tschugaeff, *Ber.*, **31**, 360, 1775, 2451 (1898).

[8] Brauns, This Journal, **45**, 833 (1923).

(see experimental part). Chlorotetra-acetylfructose has been previously[9] prepared.

The results[10] of comparison of the fluoro, chloro, bromo and iodo derivatives are presented in Table II, which shows that the data agree with the results of previous investigators in failing to support Guye's hypothesis. The increase in rotation from the fluorine to the chlorine derivative is much greater than the other differences, whereas the increase in atomic weight from fluorine to chlorine is much smaller than the others. The deviations found here immediately suggest a relationship with the atomic *diameters*. W. L. Bragg[11] derived these from the distances of the alternating atoms in the cubical crystals of the alkali halides. Bragg found that "the substitution of chlorine by bromine or bromine by iodine increases the distances between atomic centers by an amount which is approximately the same throughout the series of compounds, as the figures in italics show." Table I shows the results of Bragg's investigation.

TABLE I[12]

INTERATOMIC DISTANCES IN HALIDES, IN ÅNGSTROM UNITS (10^{-8} CM.)

	United with		
	Na	K	Rb
F	2.39	2.73	
	.42	.40	
Cl	2.81	3.13	3.28
	.16	.15	.16
Br	2.97	3.28	3.44
	.26	.24	.22
I	3.23	3.52	3.66

For convenience we will take as an average for these increases 41, 16, and 24×10^{-10} cm. These values have been compared with the increase in optical rotation from the fluorine to the chlorine derivatives, etc., in Tables III and IV; the last column of Table III shows the differences

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[9] THIS JOURNAL, **42**, 1846 (1920).

[10] In addition to fluorotetra-acetylfructose and the fluoro-acetyl sugar derivatives previously described (THIS JOURNAL, **45**, 833 (1923)) the author has prepared other fluoro-acetyl derivatives of other sugars; however, in the case of these latter derivatives, the other halogen derivatives necessary for comparison are not available. The preparation and properties of these latter fluorine derivatives will be reported later.

[11] Bragg, *Science Progress*, **16**, 45 (1921).

[12] These figures are *dimensions of ions*, which have the outer shell of electrons complete, as in the case of the inert gases. No doubt these figures are equally applicable for the dimensions of the *neutral atoms* of the halogens. It is realized that these values are not final, nor do they agree exactly with those determined by other workers using different methods or holding different theories of atomic arrangement or structure. However, there seems to be no expectation, from the writings of many workers along this line, that it will be found that these values are not approximately correct. Even a critic of Bragg's views [Wyckoff, *Proc. Nat. Acad. Sci.*, **9**, 33–8 (1923)] gives values for the diameters of F, Cl, Br and I the differences between which are in the ratio of 41:15:23, that is, not materially different from those adopted in this paper.

in atomic dimensions, reduced to approximately the same numerical values as those of the preceding columns.

Table II

Comparison of Specific and Molecular Rotations with Atomic Weight

	Glucose derivatives				Cellose derivatives					
	Spec. r.	Diff.	Mol. r.[a]	Diff.	Spec. r.	Diff.	Mol. r.	Diff.	At. wt.	Diff.
Cl	165.8		608		74.5		488		35.5	
		32.3		206		21.5		183		44.4
Br	198.1		814		96		671		79.9	
		34		244		29.5		265		47.0
I	232		1058		125.5		936		126.9	

[a] The molecular rotations are divided by 100.

Table III

Comparison of Specific Rotations with Atomic Diameters

	Derivatives of				Respective spec. rot. diff.				At. diam. diff. reduced[b]			
	Glucose	Cellose	Xylose	Fructose								
F	+ 90.1	+ 30.0	+ 67.2	− 90.4								
					76	45	98	71	76	45	98	71
Cl	+165.8	+ 74.5	+165	−160.9[a]								
					32	21	47	28	30	18	38	28
Br	+198.1	+ 96	+212	−189.1								
					34	30	..	..	44	26	..	..
I	+232	+125.5	...	....								

[a] The α-Cl derivative is taken, since we have to deal here with negative rotations [This Journal, **41**, 1849 (1920)].

[b] Starting with the (F-Cl) rotation-difference for each sugar the other values given are to one another as 41:16:24 (Table I).

Table IV

Comparison of Molecular Rotations with Atomic Diameters

	Derivatives of				Respective mol. rot. diffs.				At. diam. diffs.
	Glucose	Cellose	Xylose	Fructose					
F	+ 315	+191	+186	−315					
					293	297	300	274	41
Cl	+ 608	+488	+486	−589					
					206	183	233	188	16
Br	+ 814	+671	+719	−777					
					249	265	...	...	24
I	+1063	+936	...	...					

The following conclusions are derived from examination of these tables.

1. The differences in specific rotations vary in parallel manner with the differences in atomic diameters. Whereas the differences themselves are for the heavier cellose derivatives smaller and for the lighter xylose derivatives larger than for the glucose derivatives, they are nevertheless in all cases approximately proportional to the differences of the atomic diameters.

2. Atomic dimensions may well play a role in physical constants

pertaining to volume (specific gravity, solubility, refraction, etc.) as A. Sommerfeld[13] suggests. In the case of optical rotation, however, the relationship is less apparent. We may suppose that the distance between the halogen and the carbon atom is the determining factor; in this case it is strange, however, that the atomic weight is not more directly involved. It may be that the atomic dimension is an expression of the rotational momentum of the moving electrons in the atom. Unexpected is the result that the specific and not the molecular rotation is related to the atomic diameter in this simple way. After all, the nature of the action of a *molecule* on the light still remains to be determined. We have probably to interpret the results by supposing that the dimension of the halogen atom combined with the dimensions of the other asymmetric groups determines the *asymmetric character* of the molecule, and that the molecule by its entire weight (or with its total number of positive and negative electrons) brings its asymmetry to act upon the light.

Other relations in which atomic dimensions seem to play a role were observed by examination of the literature. In Tables V, VI and VII the author has inserted the values of the atomic diameter for purpose of comparison with the data quoted.

Chemical Affinity or Reaction Velocity

Holleman[14] and co-workers determined quantitatively the amounts of[15] *o*- and *p*-nitrohalogenbenzene which are formed by nitrating monohalogenbenzene. The results are given in Table V.

TABLE V

COMPARISON OF ATOMIC DIAMETER AND THE FORMATION OF NITROHALOGENBENZENES

	Ortho %	*Para* %	Difference in % *ortho* derivs.	$\frac{\textit{Ortho}}{\textit{para}}$	Successive diffs. in $\frac{\textit{ortho}}{\textit{para}}$	Diff. in at. diam. reduced	
F	12.6	87.4		0.14			
			17.5		29	17.5	29
Cl	30.1	69.9		.43			
			7.5		17	6.8	11
Br	37.6	62.4		.60			
			3.5		10	10.2	17
I	41.1	58.7		.70			

It is remarkable that the difference F-Cl is again much larger than Cl-Br. This suggests a relation to atomic dimensions. The difference Br-I does not agree with this assumption; the investigation of these iodine derivatives may, however, be subject to error owing to the possibility of secondary

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[13] Sommerfeld, "Atombau und Spektrallinien," 3rd ed., **1922**, Vieweg (Braunschweig) p. 132.

[14] Holleman, *Rec. trav. chim.*, **32**, 139 (1913).

[15] The *meta* compound is produced only in traces.

reactions. Results of Lulofs[16] who investigated a somewhat similar subject, measuring the velocity of substitution of halogen by an oxyalkyl group in halogen dinitrobenzenes, appear also to indicate that Holleman's results may be complicated by secondary reactions. Lulofs found the respective values 3.26, 1.89 and 0.455 for the chlorine, bromine and iodine derivatives; his data show for the difference Br-I a slightly greater value than for Cl-Br.

Boiling Points and Molecular Volumes of Corresponding Halogen Derivatives

Beekman[17] determined the boiling points of the members of a series of corresponding halogen derivatives. Most of the molecular volumes were determined by interpolation from existing data and are, therefore, according to the author, only approximately correct. His results are compared with atomic dimensions in Table VI.

TABLE VI

DIFFERENCES IN BOILING POINTS AND MOLECULAR VOLUMES OF HALOGEN DERIVATIVES

	Diff. in b. p.	Diff. in mol. vol.	Diff. in at. diam.	Reduced
C_6H_5F				
	46.5	7.84	46.5	7.8
C_6H_5Cl				
	25.1	3.68	18.1	3.0
C_6H_5Br				
	31.76	6.04	27.2	4.6
C_6H_5I				
	Meta Derivatives			
$C_6H_4FNO_2$				
	30.6	8.2	30.6	8.2
$C_6H_4ClNO_2$				
	20.9	4.25	13.0	3.2
$C_6H_4BrNO_2$				
	23.5	8.1	17.9	4.8
$C_6H_4INO_2$				
	Para Derivatives			
$C_6H_4FNO_2$				
	37	8.61	37	8.6
$C_6H_4ClNO_2$				
	14	4.93	13	3.4
$C_6H_4BrNO_2$				
	..	6.89	..	5.0
$C_6H_4INO_2$				

The agreement with difference in atomic diameters is better for the boiling points than for the molecular volumes. Both values show, however, the exceptional place taken by the fluorine derivatives, as Beekman has already observed.

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[16] Lulofs, *Rec. trav. chim.*, **20**, 292 (1901).

[17] Beekman, *Rec. trav. chim.*, **23**, 144 (1904).

Atomic Refraction

Swarts[18] has determined the atomic refraction of several saturated and unsaturated compounds containing fluorine, chlorine and bromine. Table VII shows the results of this investigation, the numerical values of the atomic dimensions being reduced.

TABLE VII

COMPARISON OF ATOMIC REFRACTION INDICES WITH ATOMIC DIAMETERS

	Sat. compds.	Unsat. compds.	Diffs.		Diff. at. diam. reduced	
F	1.082	0.775				
			4.8	5.2	4.8	5.2
Cl	5.9028	6.001				
			2.8	2.7	1.9	2.0
Br	8.762	8.759				

The agreement is not very striking, but shows that the difference in atomic refraction for Cl-F is nearly twice as great as for Br-Cl.[19]

As has already been observed, the correlation of molecular volume and refraction with atomic dimension is not unexpected. Furthermore, the relative quantities of *ortho* and *para* derivatives which are formed in a reaction can be conceived to be dependent upon the atomic dimension (in this case, the influence of the distance of the halogen from the carbon atom). The relationship of specific rotation and atomic dimension suggests, however, the possibility that atomic dimension may also play an important role in a number of physical and chemical properties which are not supposed to be influenced by this factor.[20]

[18] *Bull. acad. roy. med. Belg.*, [3] **34,** 293 (1897).

[19] Heydweiller [*Ber. physik. Ges.*, **16**, 722 (1914)] has compiled the atomic-refraction data for nearly all elements existing in solution in ionized condition. The values for the halogens (values for F and Cl are not very accurate) give the ratio (Cl—F):(Br—Cl):I—Br) = 5.6:3.5:5.9, which shows that the (I—Br) value is decidedly too high for the atomic dimension relationship. It is possible that some complicating factor is involved.

While this paper was in the hands of the reviewing committee, another paper by Swarts has come to the writer's attention [*J. chim. phys.*, **20,** 30 (1923)] in which comparisons are made between atomic refraction and the same atomic-diameter values taken from Bragg which have been used in the present paper. Swarts found almost exact agreement in the case of the three heavier halogens, although fluorine showed considerable deviation.

[20] The investigation of optical rotation from this point of view will be continued for other types of halogen derivatives; such derivatives, representing four different sugar groups,—an aldohexose, a pentose, a disaccharide, and a ketose,—have already been tested. It is probable that further investigation will throw more light on the specific influence of the medium, concentration, etc., on the optical rotation; in the case of the sugar derivatives discussed in the present paper this influence is, however, relatively small as compared with the large differences in specific rotation. Other groups of related elements, such as (oxygen), sulfur, selenium and tellurium, may be examined in view of the fact that methods for obtaining corresponding sugar derivatives containing these elements (S and Se) are available. The derivatives already reported [Schneider and coworkers, *Ber.*, **52,** 2135 (1920), Wrede, *Z. physiol. Chem.*, **115,** 284 (1921), and many others of earlier date] do not permit a comparison.

Experimental Part

Fluorotetra-acetylfructose.—Starting with β-penta-acetylfructose[21] the manner of preparation of this compound is the same as that described by the author for fluorotetraacetylglucose.[3] The resulting colorless sirup crystallized readily when stirred with petroleum ether. Ten g. of β-penta-acetylfructose yielded about 7 g. of impure product. It was recrystallized by dissolving in 30 cc. of hot, 95% alcohol, filtering and washing the filter with about 15 cc. of hot alcohol. Crystals of moderate size were obtained; yield of pure substance, about 5 g.; m. p., 112°. A second and third recrystallization gave practically identical specific rotations. After the second recrystallization, 1.4803 g. made up to 25 cc. in chloroform produced a rotation in a 2dm. tube of 10.709 circular degrees to the left; hence, $[\alpha]_D^{20} = -90.43°$. The compound is stable, colorless, odorless, and has a bitter taste; it is very slightly soluble in petroleum ether, slightly soluble in alcohol, and readily soluble in chloroform.

Analyses.[22] Subs., 0.2151: CO_2, 0.3783; H_2O, 0.1046. Subs., 0.5819: CaF_2, 0.0620. Subs., 0.5378: 219.3 cc. of 0.1 N NaOH; 142.39 cc. of 0.1 N H_2SO_4. Subs., 1.8670, 3.6201, 5.1018: C_6H_6, 100; ΔF, 0.276°, 0.215°, 0.728°. Calc. for $C_{14}H_{19}O_9F$: C, 47.98; H, 5.47; F, 5.43; 68.60 cc. of 0.1 N NaOH for AcOH; mol. wt., 350. Found: C, 47.97; H, 5.44; F, 5.19; 68.32 cc. of 0.1 N NaOH; mol. wt., 338, 347, 350.

Bromotetra-acetylfructose.—The preparation of this compound requires much care. At ordinary temperature it decomposes quickly, and special arrangements were required for analyzing and measuring the optical rotation of the pure substance. On account of the theoretical considerations involved, the attempt to prepare it which had been unsuccessfully made on previous occasions was resumed and finally led to the preparation of the pure crystalline substance and measurement of its rotation, as the excellent figures obtained on analysis show.

Six g. of powdered β-penta-acetylfructose was dissolved in 7 cc. of glacial acetic acid in a 25cc. volumetric flask with accurately ground stopper, by slightly warming the mixture on the steam-bath, the solution being then cooled in cracked ice to about 0°. A saturated solution of hydrogen bromide in glacial acetic acid was cooled in an ice-and-salt bath in a tube with ground stopper. This cold solution was used for quickly completing the volume of the fructose penta-acetate solution to about 25 cc., after which the stopper of the volumetric flask was replaced and the sirupy contents mixed by rotating the flask, the latter being kept in cracked ice for one hour. The solution was poured into about 30 cc. of chloroform[23] which had been cooled in an ice-and-salt bath in an Erlenmeyer flask with ground stopper. Without rinsing out the volumetric flask, the chloroform solution was poured in a mixture of ice water, cracked ice and a small amount of chloroform, contained in a separatory funnel.[24] The mixture was shaken and the chloroform solution drawn off into another separatory funnel and again shaken. This procedure was repeated twice, washing being omitted in order to permit more rapid work. The chloroform solution was dried over anhydrous sodium sulfate in an Erlenmeyer

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[21] THIS JOURNAL, **37**, 1283 (1915).

[22] For description of methods of analysis, see Ref. 8, p. 835. Saponification was performed by shaking with NaOH solution for 8½ hours at 0° and titrating with H_2SO_4 and phenolphthalein.

[23] The $CHCl_3$ had been specially purified by shaking it with some water, drying over Na_2SO_4, and distilling, the first and last fractions of the distillate being discarded.

[24] Two separatory funnels were made ready in this manner before the preparation of the compound was commenced. Arrangements for the Carius and acetyl determinations and for combustion were also made in advance, the only subsequent manipulation required being the introduction of the weighed substance.

flask (with ground stopper) in an ice-and-salt bath. After drying for about 1/4 hour, the solution was filtered into a crystallizing dish and evaporated under a glass jar by means of a rapid current of air. The solution was cooled below 0° by this rapid evaporation. A pure white crystalline preparation was obtained.[25] A few cubic centimeters of absolute ether were stirred with the crystals and they were then pressed between hardened paper. The yield was more than 4 g. of pure substance. Taking into account the manner of preparation, the reaction probably gives a quantitative yield. The 4 accurate weighings necessary for combustion, Carius determination (including sealing of tube), acetyl determination, and preparation of the chloroform solution for measurement of optical rotation (performed in order stated), were made in about 25 minutes and gave the following results.

Analyses. Subs., 0.1614: CO_2, 0.2419; H_2O, 0.0685. Subs., 0.1885; AgBr, 0.0864. Subs., 0.5522: 219.3 cc. of 0.1 N NaOH; 152.4 cc. 0.1 N H_2SO_4; AgBr, 0.2518. Calc. for $C_{14}H_{19}O_9Br$: C, 40.87; H, 4.66; Br, 19.44; 152.6 cc. of 0.1 N H_2SO_4; AgBr, 0.2518. Found: C, 40.89; H, 4.75; Br, 19.50; 152.4 cc. of 0.1 N H_2SO_4; AgBr, 0.2518.

A solution of 0.4768 g. in chloroform made up to 25 cc. about 25 minutes after the preparation was obtained, produced a rotation in a 2dm. tube of 7.070 circular degrees to the left; hence, $[\alpha]_D^{20} = -186°$. Another preparation of bromotetra-acetylfructose was examined immediately after the substance was prepared. A solution of 0.8188 g. of this preparation in 25 cc. of chloroform produced a rotation in a 2dm. tube of 12.397 circular degrees to the left; hence, $[\alpha]_D^{20} = -189.1°$; this is taken as the specific rotation of the pure substance.

The substance was quickly recrystallized by making a saturated solution in pure ether in a weighing bottle, seeding with a few crystals, closing tightly with a rubber stopper and cooling in an ice-and-salt bath. The beautiful, large crystals which separated were quickly pressed between hardened filter paper. The specific rotation of this preparation was $[\alpha]_D^{20}$ —188.3°.

Bromotetra-acetylfructose is a very unstable substance. It can be obtained in pure crystalline form, but decomposition is already noticeable at room temperature after 25 minutes. In a few hours most of it is converted into β-tetra-acetylfructose. It may be kept in a pure ether solution, or better a pure chloroform solution, at —10° overnight, but decomposition is noticeable even under these conditions. The melting point is 65°. It is colorless, odorless, has a bitter taste, and is very soluble in the usual solvents and slightly soluble in petroleum ether.

Summary

In comparing the optical rotations of monohalogen acetyl derivatives of glucose, cellose, xylose and fructose, the differences F-Cl, Cl-Br, and Br-I are found to be approximately proportional to the differences in atomic diameter recorded by Bragg. It is remarkable that this simple relation holds for the specific but not for the molecular rotation. The

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[25] While the chloroform solution was being evaporated to a thick colorless sirup (requiring about one hour), a small portion of the solution was evaporated on a watch glass, and by rubbing with a glass rod and finally adding ether or petroleum ether and subsequently evaporating, the resulting sirup was brought to crystallization. The crystals obtained were used for seeding the principal portion of the chloroform-free sirup.

method of preparation, properties, and analyses of fluorotetra-acetylfructose and bromotetra-acetylfructose are given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OHIO STATE UNIVERSITY]

THE PREPARATION AND PROPERTIES OF 1-MERCAPTO-BENZOTHIAZOLE, ITS HOMOLOGS AND DERIVATIVES[1,2]

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The present paper comprises a study of the synthesis of 1-mercapto-benzothiazole and its derivatives which was made in connection with an investigation of the role played by these compounds when functioning as accelerators of vulcanization. Eight different mercapto-benzothiazoles were prepared and studied. Each of these substances excepting where the quantity of material was limited, were prepared by four separate methods. These methods were alike in that the reaction mixture was heated in an autoclave under pressure. The reaction mixtures were as follows: (1) the corresponding disubstituted thio-urea and sulfur; (2) the zinc salt of the corresponding aryl dithiocarbamic acid and sulfur; (3) the ammonium salt of the same acid and sulfur; (4) a mixture of the corresponding aryl amine, carbon disulfide and sulfur.

The first method has been described by Romani.[3] The last three methods are new.

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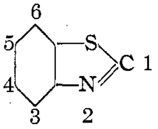
[1] This paper and one entitled: "A Study of 1-Mercapto-benzothiazole and its Derivatives as Accelerators of Vulcanization" being published in a current number of *J. Ind. Eng. Chem.* [**15**, 1009 (1923)] have been abstracted from the dissertation presented by L. B. Sebrell to the Graduate School of Ohio State University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September, 1922.

[2] The system of nomenclature as outlined in *C. A. Decennial Index*, **1-10**, 2345, namely, omitting the sulfur and beginning the numbering with the carbon atom of the thiazole ring has been followed throughout this article.



[3] The four methods of preparation described in the following pages as applied to 1-mercapto-benzothiazole and its three monomethyl derivatives, together with their disulfides and metallic salts were reported before the Organic Division of the American Chemical Society at the Birmingham meeting, April 6th, 1922. [(a) See *Science*, **56**, 55 (1922).] Shortly afterward, an article by Romani, [(b) *Gazz. chim. ital.*, **52**, 29 (1922)] became available, describing the preparation of the three methyl derivatives by one of the methods, namely, heating the corresponding disubstituted thio-urea with sulfur. To him, undoubtedly, belongs priority of publication of a description of these three derivatives by this one method. He did not describe the disulfides.