yield, 2.12 g. (36%) of white crystalline powder, m. p. 245.5–247.5° (corr.).[4] With Grote's reagent[5] a faint orange color developed only after addition of potassium cyanide, as is characteristic of monosulfides.

Anal. Calcd. for $C_{12}H_{30}Cl_2N_2S$: S, 10.53; Cl, 23.23. Found: S, 10.24; Cl, 23.31, 23.35.

bis-(β-Diethylaminoethyl) sulfide dihydrobromide was prepared similarly to the dihydrochloride as a white crystalline powder, m. p. 237.3–237.8° (corr.).

Anal. Calcd. for $C_{12}H_{30}Br_2N_2S$: Br, 40.56. Found: Br, 41.06.

(4) W. E. Lawson and E. E. Reid, THIS JOURNAL, **47**, 2821 (1925), give 247° (corr.) as the melting point of the compound prepared from β,β'-dichlorodiethyl sulfide and diethylamine.

(5) I. W. Grote, *J. Biol. Chem.*, **93**, 25 (1931).

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Relations between Rotatory Power and Structure in the Sugar Group. XXXIV. The Possibility of Different Conformations of the Pyranoid Ring[1]

BY C. S. HUDSON

In a preceding article by Eugene Pacsu[2] he suggests that the exceptional character of the rotations of the α- and β-forms of substances having the pyranoid ring structure in the mannose series may be due to a difference in the conformation of the atoms forming the ring. I thank Dr. Pacsu, with whom I have conferred often during the progress of his research, for this opportunity to publish concurrently the reasons which have led me to take the same viewpoint on this question.

In 1930[3] I expressed the view that the exceptional character of these rotations indicated that the substances had different ring structures, and I assumed that the α-forms were of the furanoid and the β-forms of the pyranoid type. The experiments of Haworth and Hirst[4] and their collaborators, designed to test this view, yielded results which showed that it is not tenable and that the substances in question possess only the pyranoid ring. From then on I have searched for an explanation of these unusual rotations that would be compatible with a pyranoid ring structure. The discovery[5] of a crystalline molecular compound of the α- and β-forms of methyl xyloside suggested the possibility that some of the supposedly pure substances of the mannose series might be compounds of this nature, an hypothesis which easily could account for the exceptional rotations. Many efforts by various ways to separate α-methyl mannopyranoside into components and similar experiments on its tetraacetate and on the tetraacetate of β-methyl mannopyranoside, led to negative results; the hypothesis of the compound nature of any of these substances thus became very improbable but nevertheless the failures did not eliminate it as a possibility. Positive proof that they are true chemical individuals, not molecular compounds, was obtained in the course of experiments[6] on the oxidation of methyl glycosides by periodic acid; their exceptional rotations, as compared with those of their glucose analogs, are not attributable either to ring-size or to any lack of chemical individuality. As was pointed out some years ago,[7] there are several differences of rotation in the mannose pyranoid series that conform closely with analogous differences in the glucose series, provided one compares substances of α-classification only, or of β-classification only. Pacsu now finds similar relationships in the fructose and sorbose pyranoid series. It would seem therefore that the agreement of rotational differences within the α- or the β-series, when coupled with the known disagreement across an α–β pair, probably indicates differences in pyranoid ring conformation.

(1) Publication authorized by the Surgeon General, U. S. Public Health Service. No. XXXIII was published in THIS JOURNAL, **61**, 1658 (1939).

(2) Pacsu, THIS JOURNAL, **61**, 2669 (1939).

(3) Hudson, *ibid.*, **52**, 1680 (1930).

(4) Haworth and Hirst, *J. Chem. Soc.*, 2615 (1930), *et seq.*

(5) Hockett and Hudson, THIS JOURNAL, **53**, 4454 (1931).

(6) Jackson and Hudson, *ibid.*, **61**, 959 (1939).

(7) Hudson, *ibid.*, **48**, 1424 (1926).

CONTRIBUTION FROM THE
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The Preparation of Seleno Ortho- and Meta-Cresols

BY DUNCAN G. FOSTER

In preparing a series of compounds for the measurement of vapor-phase absorption spectra it developed that the two compounds seleno *o*- and *m*-cresol, $CH_3C_6H_4SeH$, had never been described in the literature. The writer has prepared them by the standard method of treating the tolyl Grignard reagents with elementary selenium,[1] operating in a current of hydrogen. When hydrogen was not used no selenocresols were obtained, but only high-boiling selenides, which perhaps explains why they are not reported.

(1) Taboury, *Ann. chim. phys.*, **15**, 5 (1908).

TABLE I

PREPARATION DETAILS AND ANALYSES

Product	Starting compound	Yield G.	Yield %	M. p. or b. p. °C.	M. p. or b. p. Mm.	Physical form, color	Analysis Calcd.	Analysis Found
o-$CH_3C_6H_4SeH$	*o*-$CH_3C_6H_4Br$	85.5	35	41	99	25	Colorless		
m-$CH_3C_6H_4SeH$	*m*-$CH_3C_6H_4Br$	85.5	40	47	89	16	liquid		
o-$CH_3C_6H_4SeO_2H$	*o*-$CH_3C_6H_4SeH$	4.0	3.3	72	123–125		White needles	C 41.38 H 3.94	C 41.03 H 3.91
m-$CH_3C_6H_4SeO_2H$	*m*-$CH_3C_6H_4SeH$	7.0	5.7	96	118–119		White needles or plates	C 41.38 H 3.94	C 41.46 H 4.07

The compounds are colorless liquids when absolutely pure, but rapidly turn yellow on contact with the air. Direct analyses were found to be impracticable because their acid nature renders the Parr bomb method inapplicable and their instability and toxic properties make handling for carbon and hydrogen determinations difficult. For identification, they were converted to the acids $CH_3C_6H_4SeO_2H$[2] by dissolving in nitric acid and these compounds analyzed for carbon and hydrogen. This does not distinguish them from the ditolyl diselenides, which would behave in the same way, but the boiling points were much too low for them to have been diselenides. The copper salts were also prepared by standard means.[3] They were blue crystalline solids without m. p.

(2) Pyman, *J. Chem. Soc.*, [1] **115**, 166 (1919).
(3) Stoecker and Krafft, *Ber.*, **39**, 2200 (1906).

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Note on the Preparation of *d*-Galacturonic Acid

BY IRA A. MANVILLE, FRANCIS J. REITHEL AND PAUL M. YAMADA

In a recent article[1] there was described a method for the enzymic preparation of *d*-galacturonic acid from polygalacturonic acid. We have had the pre-publication privilege of using this method for preparing the *d*-galacturonic acid necessary for our work on its nutritional significance. It was found in our laboratory that the method, though far superior to former methods in many respects, gave varying yields. Although this in no way detracted from the excellence of the method, it posed the question as to what factors should be considered in improving the yield.

First of all we tried different pectins. Of these, there seemed to be considerable variation even between "batches." Most satisfactory in our work was General Food's Certo Apple Pectin RX 1 or 2. California Fruit Exchange Citrus Pectin, Sample B-6712, also gave good results. We are not prepared to explain why these are better, but simply state the result of empirical observations and call attention to the importance of this detail.

Secondly, we found that in the preparation of pectic (polygalacturonic) acid, it was quite necessary for the best yield to remove the last trace of the calcium chloride which we used for controlling the swelling of the pectin. This was accomplished as follows. After swelling the pectin in alcohol and calcium chloride, adding sodium hydroxide, acidifying and washing (until no precipitate resulted upon the addition of sodium oxalate or five volumes of alcohol), the resultant pectic acid was suspended again in a volume of water equivalent to that of the alcohol. About half as much sodium hydroxide was added as before. It was then acidified and washed again. The pectic acid obtained has no contamination with pectin or calcium chloride. That the concentration of calcium chloride affects enzymic action is shown by the fact that addition of calcium chloride to the enzyme–pectic acid mixture will inhibit the action of the enzyme.

Thirdly, we found that of those preparations tried, only Röhm and Haas Pectinase 46 AP seemed to yield satisfactory results. This is the enzyme contained in the preparation used by Mottern and Cole.

Several other minor points should be mentioned. After enzyme action is complete, we find it advantageous to add the sulfuric acid before filtration. Further, it is often wise to work up the sludge from the alcohol precipitation by treating it with small amounts of sulfuric acid and carrying it on in the same manner as the original material.

By carefully observing all these points in technique, we have been able to obtain yields as high as 36% of the theoretical and have had no difficulty in obtaining a very pure product which, after recrystallization in the β-form from boiling absolute alcohol, has a melting point of 160°.

The purpose of this note is to aid those using

(1) Mottern and Cole, THIS JOURNAL, **61**, 2701 (1939).