to the free acids or lactones by boiling with copper sulfate solution by which the phenylhydrazide is hydrolyzed and the liberated phenylhydrazine oxidized to benzene and nitrogen. Data from the treatment of three representative phenylhydrazides by this method show good yields with a minimum expenditure of time and effort. It is believed that the method is an improvement on the usual procedure of boiling the phenyl hydrazide with barium hydroxide, which often gives a very slow or incomplete hydrolysis.

Washington, D. C. Received January 5, 1934

[Contribution from the National Institute of Health, U. S. Public Health Service]

Improvements in the Preparation of Crystalline *d*-Mannose[1]

By C. S. Hudson and E. L. Jackson

Without doubt the best source of *d*-mannose is the vegetable ivory turnings from button factories.[2] From the acid hydrolysis of the mannan in this material mannose is generated and may be separated by the use of phenylhydrazine as mannose phenylhydrazone[3] in good yield; the sugar may then be prepared in a crystalline state[4] from the hydrazone by the use of benzaldehyde.[5] While this method is dependable it is expensive. Hudson and Sawyer[6] showed in 1917 that though mannose is difficult to crystallize, it can be obtained in good yield directly from hydrolyzed vegetable ivory by careful work and the use of glacial acetic acid as a solvent in crystallization. While much mannose has since been prepared in this direct way by various workers, experience shows that the crystallization is at times unsatisfactory. Variations in the quality of the natural vegetable ivory may perhaps be the main source of trouble. We have now sought to improve the method by first preparing pure crystalline α-methyl *d*-mannoside, which crystallizes with great ease and may be prepared[7] readily in good yield (45%) from vegetable ivory, and then converting this pure substance into mannose. From Phelps and Hudson's[8] measurement of the velocity of hydrolysis of methyl mannoside by 0.5 *M* hydrochloric acid at 98°, it is evident that the reaction should be practically complete at this temperature if one uses 2% acid and a time of four hours. We now find that such a procedure results in a 70% yield of pure crystalline mannose from the mannoside, using glacial acetic acid for crystallization. The over-all yield of crystalline sugar is thus about 30% of the vegetable ivory. The method is more reliable than any previously used and is relatively inexpensive.

Procedure.—A solution of 500 g. of pure methyl mannoside[9] in 5 liters of 2% hydrochloric acid is refluxed gently for four hours. The orange colored solution is cooled to room temperature, neutralized with about 625 g. of silver carbonate, 40 g. of activated carbon[10] added, the silver chloride and excess of silver carbonate[11] filtered off by suction and washed four times with 100-cc. portions of water. The filtrate is saturated with hydrogen sulfide, 40 g. of carbon added, the silver sulfide and carbon filtered off and washed thrice with 50-cc. portions of water. The filtrate and washings are concentrated[12] under reduced pressure in a water-bath at 55–60° to a thick sirup which is mixed thoroughly with 200 cc. of absolute ethyl alcohol by warming in the bath at 50° for a few minutes with vigorous shaking. After adding a few drops of caprylic alcohol to minimize foaming, the concentration is repeated and a second 200 cc. of alcohol is added and distilled off. Most of the colorless sirup can now be poured into a 2-liter Erlenmeyer flask and the remainder transferred by use of five 100-cc. portions of 99.9% acetic acid, shaking and occasionally warming in the 50° water-bath being required. The solution is seeded with mannose crystals, stirred and left stoppered at room temperature[13] for a day and then

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

[2] Reiss, *Ber.*, **22**, 609 (1889).

[3] Fischer and Hirschberger, *ibid.*, **22**, 3218 (1889).

[4] Van Ekenstein, *Rec. Trav. Chim.*, **15**, 221 (1896); Herzfeld, *Bull. l'assoc. chim. sucr. dist.*, **14**, 376 (1896).

[5] Herzfeld, *Ber.*, **28**, 442 (1895); de Witt, *Z. Ver. Rübenzucker-ind.*, **32**, 794 (1895).

[6] Hudson and Sawyer, This Journal, **39**, 470 (1917).

[7] Hudson, "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. VII, 1927, p. 64.

[8] Phelps and Hudson, This Journal, **48**, 503 (1926).

[9] Recrystallized methyl mannoside should be used to avoid possible difficulty in the crystallization of the sugar. One recrystallization of the crude mannoside from 80% alcohol is sufficient.

[10] Commercial activated carbon should be cleaned by digestion with hot 5% hydrochloric acid followed by thorough washing.

[11] Nearly all the silver may be recovered by customary methods.

[12] If turbidity develops the solution should be filtered before the sirupy stage.

[13] It is preferable to produce the initial crystallization at room temperature to avoid separation of the sirup, which often occurs on immediate cooling of the acetic acid solution to refrigerator temperature. The mannose usually crystallizes at room temperature; in case, however, the sirup separates, it should be remixed with the acetic acid, seeded and again left at room temperature. When the directions are followed carefully, no difficulty has been experienced in the crystallization, but if this occurs, freezing the acetic acid solution as recommended by Horton [*Ind. Eng. Chem.*, **13**, 1040 (1921)] and Clark [*J. Biol. Chem.*, **51**, 1 (1922)] may be tried, although we have not found this necessary.

for three or four days at 5°. The colorless crystals are filtered off, washed with two 50-cc. portions of glacial acetic acid, then with two 50-cc. portions absolute alcohol, air-dried for a day and then for eight hours in an 80° evacuated oven; yield, 325 g. (70%); $[\alpha]^{20}_{D}$ +14.8 (constant) in water compared with +14.6 found by Hudson and Yanovsky.[14] About half of the mannose in the mother liquor may be precipitated as a sirup by ether and reconverted into methyl mannoside, but in general this is not profitable.

Summary

The preparation of crystalline *d*-mannose from the hydrolysis of vegetable ivory by the intermediate preparation of its phenylhydrazone and its reconversion to mannose with benzaldehyde has been superseded in recent years by the direct crystallization of the sugar from the hydrolyzed material through the use of glacial acetic acid as the solvent of crystallization. This method, while often successful, is not always dependable, probably because of variations in the quality of the vegetable ivory. In a previous paper directions were given for preparing pure crystalline α-methyl-*d*-mannoside in good and regular yield (45%) from vegetable ivory. It is now shown that this pure mannoside may be used as a source for the preparation of crystalline mannose in a yield of 70%, corresponding to an over-all yield of about 30% of pure crystalline sugar from vegetable ivory. It is believed that this method is the most suitable at the present time for preparing pure mannose.

WASHINGTON, D. C. RECEIVED JANUARY 6, 1934

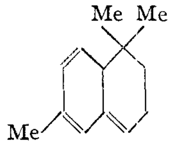
[14] Hudson and Yanovsky, THIS JOURNAL, **39**, 1022 (1917).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

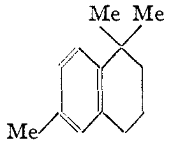
The Synthesis of Condensed Polynuclear Hydrocarbons by the Cyclodehydration of Aromatic Alcohols. II.[1] The Synthesis of Ionenes[2]

BY MARSTON T. BOGERT, DAVID DAVIDSON[3] AND P. MAX APFELBAUM

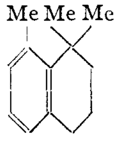
In a recent article, Bogert and Fourman[4] submitted evidence that the hydrocarbon ionene, obtained by the dehydration of either alpha- or beta-ionone, does not possess the structure (I) originally assigned to it by its discoverers, Tiemann and Krüger,[5,6] but is probably the 1,1,6-trimethyltetralin (II), as suggested in 1896 by Barbier and Bouveault.[7]



I



II

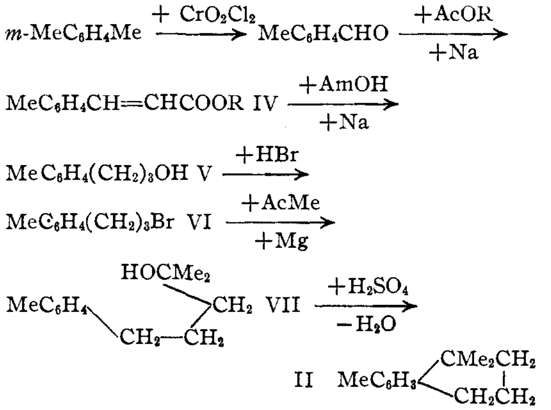


III

This formula (II), deduced experimentally by Bogert and Fourman, has now been established by the synthesis of ionene from *m*-xylene.

As reported in our preliminary announcements in *Science*,[8] the steps in this synthesis were the following:

SYNTHESIS OF IONENE



$$m\text{-MeC}_6\text{H}_4\text{Me} \xrightarrow{+\,\text{CrO}_2\text{Cl}_2} \text{MeC}_6\text{H}_4\text{CHO} \xrightarrow[+\text{Na}]{+\text{AcOR}}$$

$$\text{MeC}_6\text{H}_4\text{CH}{=}\text{CHCOOR IV} \xrightarrow[+\text{Na}]{+\text{AmOH}}$$

$$\text{MeC}_6\text{H}_4(\text{CH}_2)_3\text{OH V} \xrightarrow{+\text{HBr}}$$

$$\text{MeC}_6\text{H}_4(\text{CH}_2)_3\text{Br VI} \xrightarrow[+\text{Mg}]{+\text{AcMe}}$$

$$\text{MeC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{C(OH)Me}_2 \text{ VII} \xrightarrow[-\text{H}_2\text{O}]{+\text{H}_2\text{SO}_4}$$

$$\text{II}\quad \text{MeC}_6\text{H}_3\begin{cases}\text{CMe}_2\text{CH}_2\\ \text{CH}_2\text{CH}_2\end{cases}$$

The final step (cyclodehydration) in this series was the critical one, for it was obvious that the side chain might attach itself to the tolyl nucleus either para or ortho to the methyl group, giving in the former case ionene and in the latter the isomeric 1,1,8-trimethyltetralin (III). When the experiment was carried out, the product proved to be identical with ionene in its physical and chemical properties, and there was no evidence

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[1] I. THIS JOURNAL, **56**, 185 (1934).

[2] Presented in abstract before the Division of Organic Chemistry, at the Washington Meeting of the American Chemical Society, March 29, 1933.

[3] Research Assistant, Department of Chemistry, Columbia University.

[4] Bogert and Fourman, THIS JOURNAL, **55**, 4670 (1933).

[5] Tiemann and Krüger, (a) *Ber.*, **26**, 2675, (b) **26**, 2693 (1893); (c) **31**, 808 (1898).

[6] Tiemann (a) British Patent 8736 (May 1, 1893); (b) 17,539 (Sept. 18, 1893); (c) *Ber.*, **31**, 873 (1898).

[7] Barbier and Bouveault, *Bull. soc. chim.*, [3] **15**, 1008 (1896).

[8] Bogert, (a) *Science*, [N. S.] **76**, 475 (1932); (b) **77**, 197 (1933).