benzphenanthrene and its derivatives, and to 1,2,3,4-dibenzphenanthrene.

1,2-Dimethyl-3,4-benzphenanthrene, a new compound of interest as a potential carcinogenic agent, has been prepared in this way.

REHOVOTH, PALESTINE RECEIVED JANUARY 31, 1947

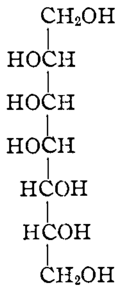
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Identification of Emil Fischer's "Phenyl-volemosazone" as D-Mannoheptose Phenylosazone

BY W. T. HASKINS AND C. S. HUDSON

In a recent review[1] one of us pointed out that it was not possible to decide from available data the configuration of the phenylosazone (melting at 196° with decomposition) which Emil Fischer[2] obtained from the products of the oxidation of the naturally occurring volemitol by sodium hypobromite. He named the substance "phenyl-volemosazone" and proved by its analysis that it belongs in the heptose series, and that accordingly volemitol is a heptitol. A decision concerning the last question was the object of this investigation.

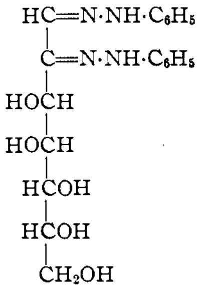
The configuration of volemitol is now known (I) and it has become evident in consequence that if "phenyl-volemosazone" is a normal osazone, as is highly probable, its configuration is limited to that of D-mannoheptose phenylosazone (II) or D-altroheptose phenylosazone (III). The formulas II and III are written in the usual form that shows solely the fundamental configuration, devoid of indications of rings that may possibly be present.



$$\begin{array}{c} CH_2OH \\ | \\ HOCH \\ | \\ HOCH \\ | \\ HOCH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ CH_2OH \end{array}$$

(I)

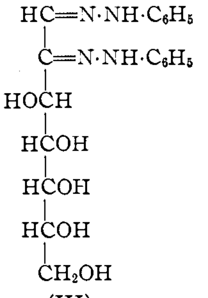
D-Volemitol (D-Manno-D-*talo*-heptitol, *syn.* D-altro-D-*manno*-heptitol)



$$\begin{array}{l} HC{=}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ C{=}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ HOCH \\ | \\ HOCH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ CH_2OH \end{array}$$

(II)

D-Manno-heptose phenylosazone



$$\begin{array}{l} HC{=}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ C{=}N{\cdot}NH{\cdot}C_6H_5 \\ | \\ HOCH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ CH_2OH \end{array}$$

(III)

D-Altro-heptose phenylosazone

Recently we have had occasion to prepare considerable quantities of the phenylosazones II and III in the course of a study of the preparation of phenylosotriazoles from them,[3] and it has become evident that, while the melting points of these phenylosazones are too nearly alike for purposes of identification, their rotations clearly lead to a distinction. With the monomethyl ether of ethylene glycol (methyl Cellosolve) as solvent, one of them (III) is strongly levorotatory and exhibits no mutarotation, whereas the other (II) is strongly dextrorotatory with a large, though slow, mutarotation to an end value that is still a dextrorotation (see Table I). These data have now been applied for the purpose of establishing the configuration of Fischer's "phenyl-volemosazone." We followed precisely the detailed directions of Fischer for oxidizing volemitol with sodium hypobromite, for obtaining a phenylosazone from the oxidation products, and for recrystallizing the crude phenylosazone. From 10 g. of pure volemitol (m. p. 153°) there was obtained 1.5 g. of crude phenylosazone, which is near the yield that he reported. Our substance proves to be D-mannoheptose phenylosazone (see Table I). Although an assumption that some D-altroheptose phenylosazone was produced during the reactions is hardly avoidable, we did not detect any of this substance in the crude phenylosazone that crystallized from the complex reaction mixture, and one recrystallization sufficed to bring the substance to full purity. These facts lead us to believe that the same phenylosazone crystallized in Fischer's experiment and that his "phenyl-volemosazone" was D-mannoheptose phenylosazone. The customary measurements of melting points are recorded in the table but it should be remembered that these osazones decompose on melting; the mixed melting points fairly confirm the identification but the rotation measurements are the real basis for it. The amount of our material did not suffice for the preparation of a phenylosotrizole in the volemitol series but this appears unnecessary in view of the definitive data from the rotations.

The name "volemose," which carries the final syllable that is customary in the names of sugars, was originally suggested by Fischer in a cursory way as the name of the "sugar" which gave rise to the "phenyl-volemosazone." Such chemical oxidations of polyhydric alcohols yield in general a complex mixture of reducing substances and it is evident that "phenyl-volemosazone" could have arisen from the aldose D-manno-D-*talo*-heptose, the ketose D-manno-heptulose, or from D-mannoheptosone resulting from their further oxidation. It could not have arisen from D-manno-D-*gala*-heptose in such experiments because the configura-

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[1] Hudson, in "Advances in Carbohydrate Chemistry," Vol. I, Academic Press Inc., New York, 1945, p. 32.

[2] Fischer, *Ber.*, **28**, 1973 (1895).

[3] Haskins, Hann and Hudson, THIS JOURNAL, **69**, 1050 (1947).

TABLE I

DATA ESTABLISHING THE IDENTITY OF "PHENYL-VOLEMOSAZONE" WITH D-MANNOHEPTOSE PHENYLOSAZONE

Substance	Melting point		Mixed melting point		$[\alpha]^{20}D$ in methyl Cellosolve
	Older literature	Present measurements	With "phenyl-volemosazone"	With D-altroheptose phenylosazone	
D-Altroheptose phenylosazone	197°[a]	194–195°	183–185°	......	−54.4° (no mutarotation during 120 hours)
"Phenyl-volemosazone"	196°[b]	194–195°	......	183–185°	+55.4° → +17.0° (96 hours)
D-Mannoheptose phenylosazone	About 200°[c]	199–200°	194–195°	185–187°	+55.9° → +17.2° (96 hours[d])

[a] LaForge and Hudson, *J. Biol. Chem.*, **30**, 61 (1917). [b] Fischer (ref. 2). [c] Fischer and Passmore, *Ber.*, **23**, 2226 (1890). [d] The mutarotation was still proceeding after forty-eight hours but had reached completion at ninety-six hours. It is so slow that the initial rotation can be measured easily.

tion of volemitol excludes this sugar. In later years Ettel[4] has suggested that "volemose" is identical with the naturally occurring ketose sedoheptulose (D-altroheptulose), but this inference proves to be unsound.

While "phenyl-volemosazone" is the useful trivial name of a definite crystalline substance, the place of which in the system of carbohydrate formulas is now established, it appears to us that the name "volemose" is inherently so indefinite that it should be discarded or used only in a historical way. On the other hand, the name "volemulose," which Bertrand[5] gave to a sirupy ketoheptose product that he made by the biochemical oxidation of volemitol with the organism *Bacterium xylinum* (classified at the present time as (*Acetobacter xylinum*) and assumed to be a single sugar because of the known specificity of action of this organism, may indeed prove to be an early name of D-mannoheptulose or D-altroheptulose. A repetition of Bertrand's experiment, which we plan to undertake, is required before a decision can be made, since Bertrand's rule of specificity for this organism indicates that either or both of these ketoheptoses could be expected from volemitol. The melting point which he reports for "phenyl-volemulosazone" (205°) apparently excludes the possibility that it was a mixture of the phenylosazones from the two sugars (see Table I).

We thank Dr. Raymond M. Hann and Mr. John Sipes for supplying the volemitol, which they prepared from sedoheptulose by reduction with sodium amalgam.

Summary

Emil Fischer's directions for preparing from the naturally occurring volemitol the crystalline substance which he named "phenylvolemosazone" have been repeated and the crystalline product which we have obtained in about the yield that he reported proves to be D-mannoheptose phenylosazone.

BETHESDA, MARYLAND RECEIVED FEBRUARY 5, 1947

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(4) Ettel, *Collection Czechoslov. Chem. Commun.*, **4**, 519 (1932); Tollens-Elsner, "Kurzes Handbuch der Kohlenhydrate," 1935, p. 405; Beilstein's "Handbuch," 4th ed., vol. 31, 1938, p. 363.

(5) Bertrand, *Compt. rend.*, **126**, 764 (1898); *Bull. soc. chim.*, [3] **19**, 348 (1898); *Ann. chim.*, [8] **3**, 209, 287 (1904).

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY, AND FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Elementary Composition of Lignin in Northern Pine and Black Spruce Woods, and of the Isolated Klason and Periodate Lignins[1]

BY W. J. WALD,[2] P. F. RITCHIE[3] AND C. B. PURVES

At the present time most investigators believe that lignins isolated from woods consist in great measure of oxygenated phenylpropane units condensed together in an unknown way to an undetermined extent. The very substantial evidence for this view has been adequately summarized by Freudenberg,[4] Hibbert,[5] Percival,[6] Phillips[7] and others. It is also agreed that chemical changes occur in lignin during its isolation from wood by acidulated alcohols, thioalcohols or phenols, by strong mineral acids or alkalies, by sulfite solutions or by many other reagents. Such changes are probably greatly increased when elevated temperatures are required for the isolation, as in technical wood pulping processes. The general

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(1) Presented at the Atlantic City meeting of the American Chemical Society, April, 1946.

(2) The results with Northern Pine wood are from a thesis submitted by W. J. Wald to the Faculty of the Massachusetts Institute of Technology in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1940.

(3) The results with Black Spruce wood were obtained by P. F. Ritchie, Gottesman Foundation Scholar, in 1945, at McGill University.

(4) Freudenberg, *Ann. Rev. Biochem.*, **8**, 88 (1939).

(5) Hibbert, *ibid.*, **11**, 183 (1942); *Paper Trade J.*, **113**, 35 (July 24, 1941).

(6) Percival, *Ann. Repts. Chem. Soc.*, **39**, 142 (1942).

(7) Wise, "Wood Chemistry," Reinhold Publishing Corp., New York, N. Y., 1944, review chapters by M. Phillips, pp. 272–368.