NOTE

Mannitol from Haplophyton Cimicidum.—During the course of an investigation of the reported insecticidal properties of the plant *Haplophyton Cimicidum*, mannitol was isolated and identified. The crude crystalline material, separating from the concentrated alcoholic extract of this plant, from which pure mannitol was obtained, represented approximately 0.75% of the weight of the plant on a dry basis. The substance was identified by means of its tribenzacetol and hexacetyl derivatives.

INSECTICIDE DIVISION OF THE
BUREAU OF CHEMISTRY AND SOILS
UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND

N. L. DRAKE
JOSEPH R. SPIES

RECEIVED JULY 3, 1930
PUBLISHED SEPTEMBER 5, 1930

COMMUNICATIONS TO THE EDITOR

AN X-RAY EXAMINATION OF THE HIGHER NORMAL PRIMARY ALCOHOLS

Sir:

X-ray examination of the higher normal primary alcohols reveals an interesting distinction between the odd and the even carbon chain series. As is usual with such long-chain compounds, the large crystal spacing increases linearly with increasing carbon content, and in the case of the higher alcohols, when crystallized from ethyl alcohol, the long crystal spacings for the odd alcohols lie on the upper Curve, I (Fig. 1), while those for the even alcohols (above C_{16}) lie on the lower Curve, II. The point of interest is, however, that below C_{16} the spacings of the even alcohols lie

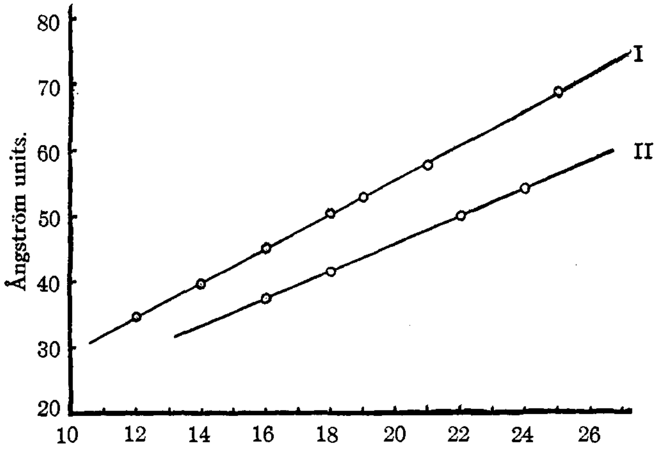

Fig. 1.

on the upper (odd) line, C_{16} alcohol itself gives two spacings, one on each line, while C_{18}, if fused, then gives a spacing on the upper line. The spacings of the odd alcohols, crystallized from solvents or fused, lie on the same upper line.

If the diameter of the carbon atom is taken as 1.54 Å., the spacings on Curve I correspond closely to a vertical chain of carbon atoms inclined tetrahedrally to each other, and those in Curve II to a similar chain tilted at an angle of 55° 40′. The vertical form is clearly a stable form for the odd alcohols and the tilted form for the even, but the latter change into the vertical form at some point below fusion. Apparently this change takes place considerably below the melting point since myristyl alcohol C_{14}, m. p. 38°, crystallized from alcohol, gives a spacing corresponding to the vertical form, and cetyl alcohol C_{16}, m. p. 49.0°, exhibits both spacings, thus indicating in the latter case that ordinary room temperature is near the transition point.

The following data were obtained using the Kα-rays of iron reflected from thin layers of the alcohols pressed or fused on a glass strip and mounted on a Müller spectrograph. The intensity distribution indicates that the alcohols crystallize in double molecules with the hydroxyl groups in juxtaposition.

X-RAY DATA FOR NORMAL PRIMARY ALCOHOLS

No. of carbon atoms	12	14	16	18	19	21	22	24	25
M. p., °C.	23.0	38.0	49.0	59.0	62.0	68.5	72.0	76.5–77	78.5
Spacing, pressed layer, Å.	..	39.7	..	41.35	52.75	57.4	49.95	54.0	68.5
Spacing, melted, layer, Å.	34.8	..	37.4 44.9	50.2	52.8	56.9	...	.....	..

It is hoped that these data will be of service to those working on the higher natural alcohols since x-ray analysis promises to afford a ready method of identification. In particular it should be useful in distinguishing between those higher alcohols of adjacent carbon content that are so difficult to identify by purely chemical means. In a subsequent paper it is hoped to give an account of the x-ray data for long-chain nitriles and iodides.

The writer wishes to express his thanks to Mr. S. H. Piper for his friendly interest in this work.

H. H. WILLS PHYSICS LABORATORY
AND THE CHEMISTRY DEPARTMENT
THE UNIVERSITY
BRISTOL, ENGLAND

T. MALKIN

RECEIVED AUGUST 4, 1930
PUBLISHED SEPTEMBER 5, 1930

THE METALLIC PRECIPITATION OF ZIRCONIUM

Sir:

The preparation of zirconium of a high degree of purity is not easy. The element combines or alloys itself with the reducing agents employed to prepare it. Probably the best method now used was devised by A. E. van Arkel and H. de Boer, who have obtained the metal by passing the vapor of the tetraiodide over a heated tungsten filament. Many metals may be prepared by precipitation from solution by a more electropositive substance than themselves. H. N. Warren[1] appears to have been the only one to employ this method for the preparation of zirconium. He states that if a rod of magnesium be wrapped with a few coils of asbestos paper and immersed in a solution of a metallic salt, the metal is precipitated on the asbestos in crystalline form. "Even zirconium was gradually reduced." This statement is erroneous, for zirconium compounds hydrolyze in water with the formation of free acid which would react with the magnesium.

It was thought, however, that zirconium might be precipitated from a solution other than aqueous. It was found that zirconium sulfate was quite soluble in methyl alcohol, the salt dissolving with a hissing sound and crystallizing out on evaporation. The alcoholic solution of zirconium sulfate was treated with metallic zinc. Hydrogen was given off, and the surface of the zinc was covered with a dark deposit. The reactions were accounted for by the equations

$$\mathrm{Zn} + \mathrm{H_2SO_4} \longrightarrow \mathrm{ZnSO_4} + \mathrm{H_2} \qquad (1)$$

$$2\mathrm{Zn} + \mathrm{Zr(SO_4)_2} \longrightarrow 2\mathrm{ZnSO_4} + \mathrm{Zr} \qquad (2)$$

Since all zirconium sulfate contains a small amount of free sulfuric acid, introduced by methods of manufacture and by hydrolysis, the presence of hydrogen may be accounted for by Equation 1. As the reaction continued, the amount of hydrogen evolved decreased until no more gas was given off. The acidity decreased proportionally until at this point it took as much as five minutes for blue litmus to turn red. When a part of the deposit was scraped off and treated with hydrochloric acid, the zinc removed along with the deposit dissolved, leaving undissolved zirconium on the bottom of the container.

When magnesium was substituted for zinc, a white precipitate of undetermined composition was formed and no zirconium was precipitated.

The inability to continue this study for some time has caused this preliminary report to be prepared.

3950 Walnut Street
Kansas City, Missouri

Howard S. Gable

Received August 6, 1930
Published September 5, 1930

---

[1] Warren, *Chem. News*, 61, 183 (1890).