compose amylose, and the value obtained for iodine absorption may be only a practical maximum and fortuitous. Packing considerations alone would allow about one iodine molecule for five glucose residues, since one molecule would require about 6.8 Å. along the helix. Furthermore, it is hard to understand why reflections of the type $(00h_3)$ are absent if the iodine molecules are spaced 7.91 Å. apart along the helix. It seems possible that their arrangement is at random in a set of six equivalent positions per turn in the helix, giving rise to an effective sixthing of the spacing along the c axis. Unfortunately, the temperature factor for the complex is so high that the reflection (006) could not possibly be observed at room temperature. This leaves the space group in doubt.

Summary

1. The amylose-iodine complex has a hexagonal unit cell, $a_0 = 12.97$, $c_0 = 7.91$, $d_{100} = 11.23$ Å.

2. The unit cell confirms a helical structure for the starch–iodine complex; 12.97 Å. is the diameter of the helix, 7.91 Å. is the length of a turn in the helix. These dimensions are in good agreement with the dimensions of a space-filling model of a helix with six glucose residues per turn.

3. The starch–iodine complex can be prepared entirely without water or iodide ion if the starch is first put in the "V" configuration by alcohol precipitation.

4. Starch in the "V" configuration will absorb iodine vapor in quantity, while in the "A" and "B" configuration it will not. Amylose in the "V" configuration will absorb 26% of its own weight in iodine. This corresponds to one iodine for six glucose residues, but it is not established that this is the maximum iodine absorption.

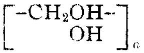
Ames, Ia. Received April 17, 1943

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

End Group Structure of Polyvinyl Alcohol[1]

By C. S. Marvel and G. Esler Inskeep

The recurring unit in polyvinyl alcohol has been shown to be that indicated in Formula I and the



$$\left[-CH_2OH- \atop \quad OH\right]_n$$

I

chemical behavior of the polymer is in general that which would be expected of a poly-1,3-glycol.[2] However, Staudinger and Warth[3] have found that alcoholysis of a given polyvinyl acetate by different methods produces specimens of polyvinyl alcohol having different properties. Blaikie and Crozier[4] have noted unusual changes in viscosity in polyvinyl acetate samples on hydrolysis and reacetylation. Also they have found that mineral acid causes polyvinyl alcohol to become insoluble. McDowell and Kenyon[5] have found that saponification of polyvinyl acetate by alcoholic potassium hydroxide followed by reacetylation by means of acetic anhydride and pyridine usually results in a reduction of chain length as measured by viscosity methods, by about one-half. Industrial experience[6] with these compounds has shown also that unusual molecular weight changes, based on viscosity determinations, on hydrolysis of polyvinyl acetates or acid treatment of polyvinyl alcohols, are not uncommon.

In the present communication are described some experiments on the hydrolysis of polyvinyl acetate samples and acid treatment of various polyvinyl alcohols in which the chain lengths measured by viscosity methods show marked changes. These changes may be in either direction depending on experimental conditions.[7]

Viscosity molecular weights and degrees of polymerization were calculated by means of the Staudinger equation using a K_m value of 2.6×10^{-4} for both polyvinyl acetate in benzene and polyvinyl alcohol[8] in water containing 2% ethanol. To solutions of polyvinyl alcohol which contained

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(1) This is the sixteenth communication on the structure of vinyl polymers. For the fifteenth, see This Journal, **65**, 1647 (1943).

(2) Staudinger, Frey and Stark, *Ber.*, **60**, 1782 (1927); Herrmann and Haehnel, *ibid.*, **60**, 1658 (1927); Marvel and Denoon, This Journal, **60**, 1045 (1938).

(3) Staudinger and Warth, *J. prakt. Chem.*, **155**, 261 (1940).

(4) Blaikie and Crozier, *Ind. Eng. Chem.*, **28**, 1155 (1936).

(5) McDowell and Kenyon, This Journal, **62**, 415 (1940).

(6) Private communication from Dr. B. C. Bren.

(7) The samples of polyvinyl acetate and polyvinyl alcohol were kindly furnished by Dr. B. C. Bren of the Plastics Department, E. I. du Pont de Nemours and Company, and we are indebted for his aid.

(8) Staudinger and Schwalbach, *Ann.*, **488**, 8 (1931).

acid, enough dilute alkali was added to make them slightly basic to litmus before viscosity measurements were made. The molecular weight values calculated from these viscosity measurements are probably valuable only for comparative purposes.

Various treatments of a given sample of polymer were carried out to determine the effect upon the degree of polymerization. The standard treatments for polyvinyl acetate samples were, (1) hydrolysis by means of methanol and sulfuric acid at reflux temperature for two hours using 0.9 mole of acid per mole of monomer unit followed by filtering, dissolving the polymeric alcohol in water, precipitating by pouring the solution into excess ethanol or acetone, decanting, washing with ethanol or acetone, filtering, washing with ether, and air-drying; and (2) saponification by treating the acetate with methyl alcoholic sodium methoxide (using 1 mole of methoxide per mole of monomer unit) for one and one-half hours, followed by isolation of the polymer and purification by washing as above.

Polyvinyl alcohol samples were given several treatments to see what the effect on chain length would be. One treatment was to boil a 5% solution in 5% sulfuric or hydrochloric acid for two hours and then isolate the polymer by diluting with four volumes of water and pouring this solution into five volumes of ethanol or acetone. Another treatment was to allow the solid polymer containing a trace of mineral acid to stand at room temperature. A third treatment was reacetylation by heating the polymeric alcohol on a steam-bath with ten times its weight of a mixture of two parts of acetic anhydride to one part of pyridine for two to twenty-four hours. Usually the polymer dissolved and it was isolated by pouring the reaction mixture into a large volume of water. This treatment seemed to cause about 80% re-acetylation.

Three samples of polyvinyl acetate were studied. All were prepared by polymerization of

CHART I

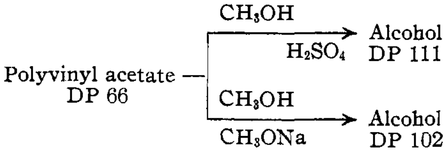


CHART II

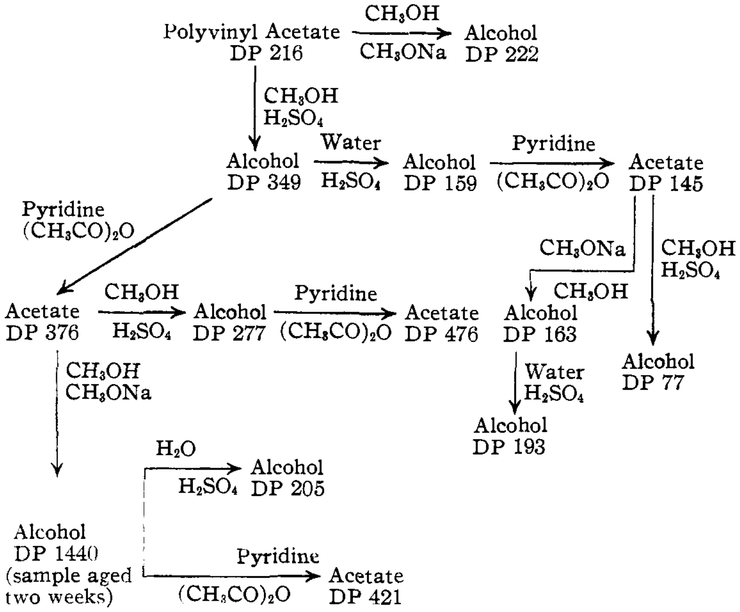
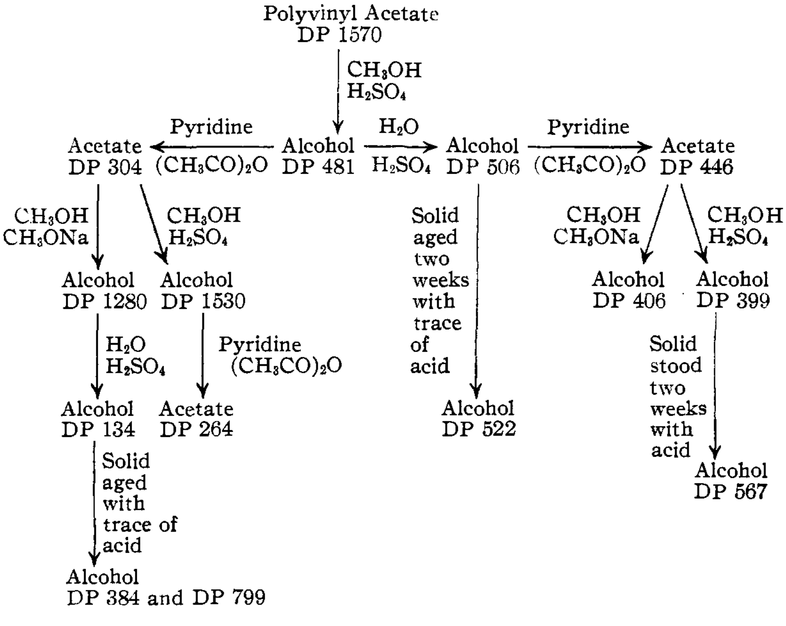


CHART III



vinyl acetate in aqueous methyl alcohol with a hydrogen peroxide catalyst. One sample had a degree of polymerization of 66, the second 216 and the third 1570. Charts I, II and III show the transformations which were carried out and the degree of polymerization (DP) of the products as calculated from viscosity measurements.

CHART IV

Polyvinyl alcohol DP 347 (Polyvinyl acetate prepared with benzoyl peroxide catalyst and hydrolyzed by CH_3ONa in CH_3OH) $\xrightarrow[H_2SO_4]{H_2O}$ Alcohol DP 342

CHART V

Polyvinyl alcohol DP 331 (H_2O_2 catalyzed and CH_3ONa and CH_3OH hydrolysis) $\xrightarrow[H_2SO_4]{CH_3OH}$ Alcohol DP 484 $\xrightarrow[H_2SO_4]{H_2O}$ Alcohol DP 261

Polyvinyl alcohol DP 331 (H_2O_2 catalyzed and CH_3ONa and CH_3OH hydrolysis) $\xrightarrow[H_2SO_4]{H_2O}$ Alcohol DP 327 $\xrightarrow[H_2SO_4]{H_2O}$ Alcohol DP 288

CHART VI

Polyvinyl alcohol DP 470 (H_2O_2 catalyzed, hydrolyzed with alcohol and sulfuric acid) $\xrightarrow[H_2SO_4]{H_2O}$ Alcohol DP 365 $\xrightarrow[(CH_3CO)_2O]{\text{Pyridine}}$ Acetate DP 483

CHART VII

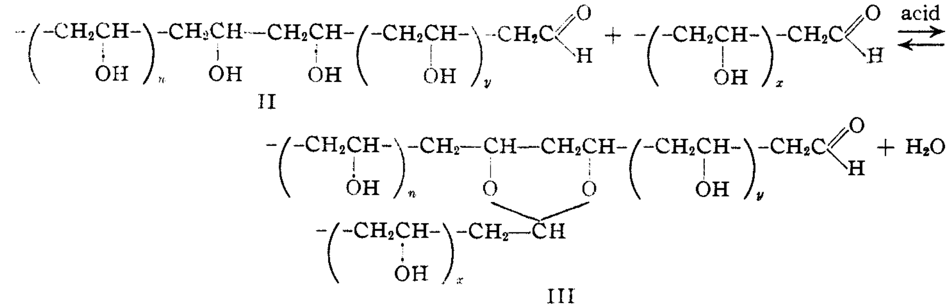
Polyvinyl alcohol DP 238 (H_2O_2 catalyzed; CH_3ONa and CH_3OH saponification) $\xrightarrow[H_2SO_4]{CH_3OH}$ Alcohol DP 506 $\xrightarrow[(CH_3CO)_2O]{\text{Pyridine}}$ Acetate DP 448

The transformations noted in the case of polyvinyl alcohol samples in various experiments are summarized briefly in Charts IV-VII.

It will be noted that in general alcoholysis of a polyvinyl acetate sample with methyl alcohol and sulfuric acid results in an alcohol with, apparently, a longer chain than was present in the ester from which it was formed. Saponification of polyvinyl acetate with sodium methoxide usually produces a polyvinyl alcohol of the same or greater chain length (degree of polymerization) than was present in the polyester. Heating a sample of polyvinyl alcohol in water with a trace of acid usually causes a reduction in chain length. A solid sample of polyvinyl alcohol containing a trace of acid is likely to increase in apparent chain length on standing. Reacetylation of such a sample usually results in formation of an ester of shorter chain length. These changes in apparent chain length are very irregular and unpredictable in amount.

A possible explanation of these changes can be given if polyvinyl alcohol has an aldehyde end group (II). Such a group would be expected to react with the alcohol groups in the same or neighboring chains to produce an acetal grouping (III).[9] The exact way in which any two molecules would combine would be largely a matter of chance, and hence viscosity molecular weight measurements, which measure chain length rather than true molecular weight,[10] would show odd results. Thus, depending on the size of n and y in Formula II, the viscosity molecular weight of III would be a different fraction of the true molecular weight. The fact that the unusual changes in apparent chain lengths occur most frequently on treatment with acids is in agreement with the idea that acetal formation is involved.

Under alkaline conditions a polymer with a terminal aldehyde group (IV) might become involved in a reversible aldol condensation to give a molecule (V) of much higher molecular weight which under different conditions could hydrolyze back to the original. Also under alkaline conditions a reverse aldol condensation might occur to cause successive removal of the terminal two-carbon unit as acetaldehyde (VI).



An aldehyde end group might be logically expected in polyvinyl alcohol and may even be expected in polyvinyl acetate. Thus, if the mechanism of chain initiation and ending involve addition of catalyst fragments a polyvinyl acetate made by hydrogen peroxide catalysis might be

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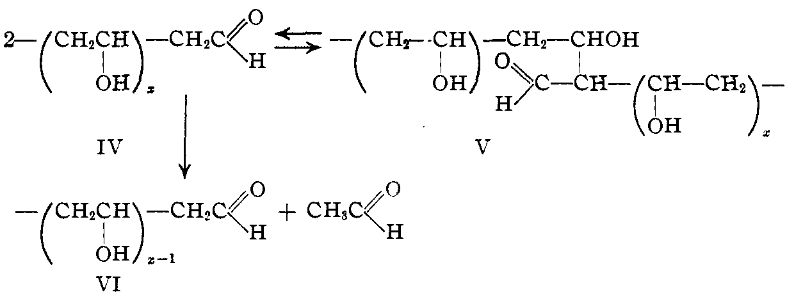
[9] Staudinger and Sohn, *Melliand Textilber.*, **21**, 205 (1940).

[10] H. Staudinger, "Die Hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932, p. 66.



$$2-\left(\mathrm{CH_2CH(OH)}\right)_x-\mathrm{CH_2CHO} \rightleftarrows -\left(\mathrm{CH_2{-}CH(OH)}\right)-\mathrm{CH_2{-}CHOH{-}CH(CHO)}-\left(\mathrm{CH(OH){-}CH_2}\right)_x-$$

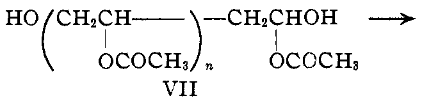
IV V

$$\downarrow$$

$$-\left(\mathrm{CH_2CH(OH)}\right)_{x-1}-\mathrm{CH_2CHO} + \mathrm{CH_3CHO}$$

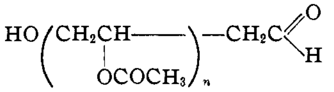
VI

expected to have the structure indicated in Formula VII or VIII.



$$\mathrm{HO}\left(\mathrm{CH_2CH(OCOCH_3)}\right)_n-\mathrm{CH_2CH(OH)(OCOCH_3)} \longrightarrow$$

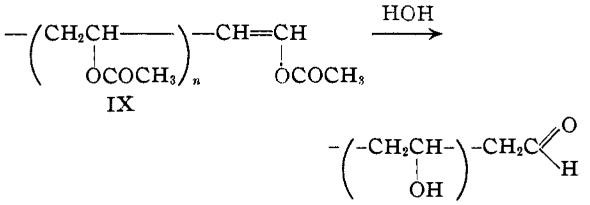
VII



$$\mathrm{HO}\left(\mathrm{CH_2CH(OCOCH_3)}\right)_n-\mathrm{CH_2CHO}$$

VIII

If the chain-ending reaction is a disproportionation the end group in polyvinyl acetate is probably an enol acetate (IX) which on hydrolysis would yield an aldehyde group (X) at the end of the polyvinyl alcohol chain.



$$-\left(\mathrm{CH_2CH(OCOCH_3)}\right)_n-\mathrm{CH{=}CH(OCOCH_3)} \xrightarrow{\mathrm{HOH}}$$

IX

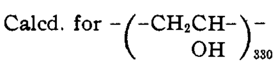
$$-\left(-\mathrm{CH_2CH(OH)}-\right)-\mathrm{CH_2CHO}$$

X

An attempt to demonstrate an aldehyde end group in polyvinyl alcohol by hypoiodite oxidation as has been done for starch molecules[11] was unsuccessful. Apparently, the secondary alcohol groups in polyvinyl alcohol are so readily oxidized as to interfere with this method. However, it has been found possible to make a 2,4-dinitrophenylhydrazone derivative of a polyvinyl alcohol having a degree of polymerization of 331 as determined by viscosity methods which has a nitrogen content indicative of a molecule containing 372 vinyl alcohol units.

Polyvinyl Alcohol 2,4-Dinitrophenylhydrazone.—A sample of polyvinyl alcohol (DP 331) was suspended in alcohol acidified with hydrochloric acid and refluxed for a few minutes with an excess of 2,4-dinitrophenylhydrazine. The polymer was then filtered and washed repeatedly with alcohol to remove all free 2,4-dinitrophenylhydrazine. The resulting polymer was dried and analyzed.

Anal. Calcd. for



$-\left(-\mathrm{CH_2CH(OH)}-\right)_{330}\mathrm{CH_2CH{=}NNHC_6H_3(NO_2)_2}$: N, 0.379. Found: N, 0.338.

This agreement in molecular weight is certainly as close as can be expected. The derivative gave the typical violet color with alkali which is characteristic of 2,4-dinitrophenylhydrazones.[12]

The absorption spectra of this 2,4-dinitrophenylhydrazone derivative of polyvinyl alcohol and the corresponding derivatives of *n*-butyraldehyde and crotonaldehyde were taken in a Coleman model 105 double monochromator spectrophotometer coupled with a Coleman model 310 electrometer using a slit width of 15 mμ and a cell thickness of 13.0 mm. The range covered was from 350–900 mμ.

These are plotted in Fig. 1 and it will be noted that there are certain definite similarities.

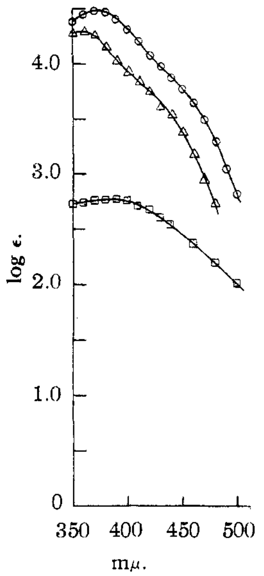


Fig. 1.—Visible absorption spectra of dinitrophenylhydrazones: O, crotonaldehyde; Δ, *n*-butyraldehyde; □, polyvinyl alcohol.

Infrared absorption spectra[13] of polyvinyl alcohol and its 2,4-dinitrophenylhydrazone were taken with films of the polymers deposited from water solution on fluoride slides. The exact thicknesses of the films were not determined but care was taken to see that they were similar. Measurements were made at the range 5.5–6.2 μ.

In the polyvinyl alcohol absorption there are two peaks (Fig. 2) in the region typical of the carbonyl group (5.8–6.2 μ).[14] One of these peaks at 5.99 μ is shown by both the polyvinyl alcohol and its 2,4-dinitrophenylhydrazone and may therefore come from

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(11) Bergmann and Machemer, *Ber.*, **63**, 316 (1930).

(12) Auwers and Kreuder, *ibid.*, **58**, 1974 (1925).

(13) We are indebted to Mr. R. M. Whitney for determining the infrared absorption spectra of our compounds and to Professor A. M. Buswell and Dr. R. C. Gore for the interpretation of these spectra.

(14) Lecomte, *Compt. rend.*, **180**, 1481 (1925); Thompson and Harris, *Trans. Faraday Soc.*, **38**, 37 (1942).

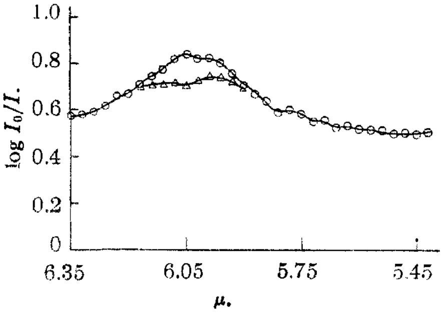

Fig. 2.—Infrared absorption spectra: O, polyvinyl alcohol; Δ, its dinitrophenylhydrazone.

some residual acetyl groups which have not been removed by saponification. The peak at 6.05 μ which is shown by the polyvinyl alcohol is greatly reduced and shifted slightly to the higher wave lengths in the derivative. This may be due to terminal carbonyl in the untreated alcohol.

It was thought possible that acid methyl alcohol might react with polyvinyl alcohol to cause some ether formation. However, Zeisel determinations on polymers treated in this manner did not show the presence of any methoxyl groups.

Summary

During the hydrolysis of polyvinyl acetate and also during reësterification of polyvinyl alcohol, unexpected and irregular changes in the apparent molecular weight of the polymer have been noted. A possible explanation of this behavior is that polyvinyl alcohol may have one terminal aldehyde group which, under acid conditions, can undergo acetal formation with the hydroxyl groups of neighboring molecules. Under alkaline conditions an aldol or reverse aldol reaction may occur to cause changes in molecular size.

URBANA, ILLINOIS RECEIVED MAY 20, 1943

[CONTRIBUTION FROM THE LABORATORIES OF CHEMISTRY AND PHYSICS, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Aldol Condensation. II. The Reaction of Isobutyraldehyde with its Aldol[1]

BY ROBERT H. SAUNDERS, M. J. MURRAY AND FORREST F. CLEVELAND

Experimental work with the aldols is complicated by the fact that even such ordinary treatment as distillation may either eliminate water to produce the unsaturated compound or dealdolize the material to the simple aldehyde. To obviate part of this difficulty the present work has been confined to 2,2,4,4-tetramethylaldol[2] (isobutyraldol) which, because of the two methyl groups in the alpha position, has practically no tendency to eliminate water during distillation. Experiments of others[3-5] which have been confirmed in the present work have shown that this aldol can be distilled without excessive dealdolization at reasonable temperatures (below 120°).

2,2,4,4-Tetramethylaldol was first obtained by Urbain[6] in 1895. Since that time a number of investigations have been undertaken to determine the nature of the condensation products formed when isobutyraldehyde is treated with alkali.[4,5,7] The results of these experiments are not in accord even for the condensation under mild conditions. According to the literature, the action of potassium hydroxide solutions at or below room temperature gives two main condensation products: a dimer that is 2,2,4,4-tetramethylaldol, and a trimer which has been identified as 2,2,4-trimethyl-3-hydroxypentyl isobutyrate. The structure of the aldol seems to have been fairly well established by means of a number of derivatives and by the ease of decomposition into isobutyraldehyde. The ester, on the other hand, has been identified by some investigators by the fact that it is converted to the salt of isobutyric acid and to 2,2,4-trimethyl-1,3-pentanediol when refluxed with alcoholic alkali. Such treatment, of course, is standard procedure for identifying esters, but it will be shown in the following discussion that in the present case the conclusions drawn from this test were not justified. Actually this isobutyraldehyde trimer may not have been the ester at all, and failure to recognize this has been the cause of much confusion not only in the condensation of isobutyraldehyde but also in the condensation of other aldehydes as well.

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(1) For the first article of this series see Saunders, Murray, Cleveland and Komarewsky, THIS JOURNAL, **65**, 1309 (1943).

(2) The aldols mentioned in this paper are systematically named as derivatives of aldol ($CH_3CHOHCH_2CHO$).

(3) Usherwood, *J. Chem. Soc.*, 1717 (1923).

(4) Grignard and Iliesco, *Compt. rend.*, **190**, 556 (1930).

(5) Kirchbaum, *Sitzb. Akad. Wiss. Wien*, IIb, **112**, 1069 (1903).

(6) Urbain, *Bull. soc. chim.*, **13**, 1048 (1895).

(7) Brauchbar, *Sitzb. Akad. Wiss. Wien*, IIb, **105**, 629 (1896).