double bonds were correct for palustric acid, one would expect to find bands due to the cis-disubstituted double bond between atoms 5 and 6 in its spectrum.

Experimental. The palustric acid employed in the study was kindly sent to the author by E. L. Patton, Head of the Naval Stores Research Section, Naval Stores Section, The United States Department of Agriculture.

The absorption spectrum was recorded with an automatic double-beam spectrophotometer of the type described by Hornig, Hyde and Adcock. The sample was examined using the potassium bromide technique. For further information, see Ref.3.

Acknowledgements. I wish to express my sincere gratitude to Dr. Ingrid Fischmeister of the Department of Medical Biochemistry for the spectrophotometric measurements and to Professor Einar StenHagen for placing the facilities of the Department at my disposal.


Received May 31, 1957.

The Formation of Anhydro Vitamin A₁ in the Study of Vitamin A₁ Isomers

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As described by Edisbury et al.1 and later by Meunier et al.2 and Schantz et al.3 the action of an anhydrous (N/30) ethanolic solution of hydrogen chloride on vitamin A₁ results in the conversion of the vitamin into the hydrocarbon anhydro vitamin A₁. Robeson and Baxter4 have shown that the two isomers 13-cis and all-trans vitamin A₁ form the same substance when treated with hydrogen chloride in ethanol, but the rate of reaction (in 0.02 N ethanolic hydrogen chloride) is not the same in the two cases.

During recent years a number of new vitamin A₁ isomers5-7 have been added to those already known, and when faced with the problem of identifying the individual components — isolated for instance by chromatography — of a mixture of vitamin A₁ isomers, it will be natural, side by side with other identification tests, to utilize the process of anhydro vitamin A₁ formation. The aim of the present work has been to develop a convenient procedure for the formation of anhydro vitamin with a view to the utilization of this reaction for purposes of identification.

It is possible to follow the course of the reaction by spectrophotometry of the reaction mixture, since the formation of anhydro vitamin A₁ causes an increase in the extinction at wavelengths above approx. 340 m, Maximum increase is observed at wavelengths of approx. 350, 368.5 and 390 m, i.e. very near the three maxima of anhydro vitamin A₁ — 351, 371, 392 m. Under the action of the hydrogen chloride solution the process continues, and anhydro vitamin A₁ is converted into iso-anhydro vitamin A₁ (maxima at approx. 330, 350 and 370 m), causing the maximum at 390 m to disappear again. The value of $E_{390}$ measured for the reaction mixture thus does not only comprise the extinction due to the anhydro vitamin A₁, but also the extinction of unconverted vitamin A₁ and iso-anhydro vitamin A₁. However, the maximum value of $E_{390}$ will almost exclusively be due to anhydro vitamin A₁.

For the purpose of following the process of anhydro vitamin formation the following two magnitudes may be used: (1) the maximum value of the ratio $E_{390} / E_{\text{max}}$ and (2) the corresponding time $t_{\text{max, ank}}$. In the ratio $E_{390} / E_{\text{max}}$ is $E_{390}$ the extinction (cell length 1 cm) of the reaction mixture at 390 m, $E_{\text{max}}$ is the extinction (cell length 1 cm) of the reaction mixture being due to vitamin A₁ at zero time, i.e. at the moment when the vitamin A₁ solution and the hydrogen chloride solution are mixed. $E_{\text{max}}$ is not measured directly, but is calculated from the value of $E_{\text{max}}$ already measured for the vitamin A₁ solution. The value of these two magnitudes, $E_{390} / E_{\text{max}}$ and $t_{\text{max, ank}}$ have been determined for all-

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trans vitamin A$_1$ at different hydrogen chloride concentrations. After mixture of for instance 2.5 ml ethanolic hydrogen chloride solution and 2.5 ml vitamin A$_1$ solution (containing about 10 $\mu$g vitamin A$_1$ per ml) the reaction mixture was poured into a quartz cuvette, and the course of the reaction was followed by measurements by means of a Beckman DU spectrophotometer. The temperature of the reaction mixture was 25–26°C.

In Fig. 1 the maximum value of the ratio $E_{360} / E_3^m$ and the corresponding reaction time have been represented as a function of the hydrogen chloride concentration in the reaction mixture. It will be seen that $(E_{360} / E_3^m)_{\text{max}}$ does not assume values above 1.18. If a further conversion of anhydro vitamin A$_1$ did not take place, complete conversion of all-trans vitamin A$_1$ into anhydro vitamin A$_1$ should be expected to result in a value of $3180 \times 268 = 1.61$ of $E_{360} / E_3^m$ [$E(1\%,$ $1$ cm, $390$ m$\mu$) = $3180$ of anhydro vitamin A$_1$, molecular weight 268, $E(1\%,$ $1$ cm, $325$ m$\mu$) = $1850$ of all-trans vitamin A$_1$, molecular weight 268].

When ethanolic hydrogen bromide (0.15 $-0.50$ N) is used, the same values of $(E_{360} / E_3^m)_{\text{max}}$ are obtained as when using 0.15 $-0.50$ N hydrogen chloride. The use of ethanolic sulphuric acid or acetic acid results in lower values of $E_{360} / E_3^m$ and higher $t_{\text{max, anh.}}$ values than those obtained with hydrogen chloride in the same molar concentration. Even 50% (v/v) acetic acid in ethanol results in a considerably slower rate of reaction with a lower value of $E_{360} / E_3^m$ than that obtained with, for instance, 0.01 N ethanolic hydrogen chloride. If anhydro vitamin A$_1$ is formed in a mixture of 1 volume of sulphuric acid (95$-97$%) and 9 volumes of absolute ethanol, $t_{\text{max, anh.}}$ is found to be about 1.0 min, while $E_{360} / E_3^m$ reaches a value of 1.04 only. Lower concentrations of sulphuric acid result in higher values of $t_{\text{max, anh.}}$ and lower values of $E_{360} / E_3^m$.

The course of the dehydration reaction for all-trans vitamin A$_1$ dissolved in ethanolic p-toluenesulphonic acid has also been examined. Schantz used p-toluenesulphonic acid as catalyst in the preparation of anhydro vitamin A$_1$. A 10% (w/v) solution of p-toluenesulphonic acid hydrate (anhydrous p-toluenesulphonic acid was not available commercially) in absolute ethanol gives $t_{\text{max, anh.}}$ = about 1 min, while $E_{360} / E_3^m$ reaches a value of about 0.5 only. Reduction of the p-toluenesulphonic acid concentration changes the course of the reaction in the same way as described with respect to the other acids.

To prepare anhydro vitamin in ethanolic solution at room temperature hydrogen chloride thus seems to be the most suitable of the dehydration agents examined in the present investigation. It may be added that the presence of merely a few per cent of water in the hydrogen chloride mixture will cause a considerable increase in $t_{\text{max, anh.}}$ and reduce the maximum value of $E_{360} / E_3^m$.

The influence of variations in the vitamin A$_1$ concentration on $t_{\text{max, anh.}}$ and $E_{360} / E_3^m$ at constant hydrogen chloride concentration has been examined for all-

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Depolymerization of 1,2-Dithiolane and 1,2-Diselenolane Polymers

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On hydrolysing trimethylendiselenocyanate, according to Hagelberg¹, Morgan and Burstall² a yellow powder is formed which was regarded as the monomer of 1,2-diselenolane (1,2-diselena-cyclopentane) by Morgan and Burstall. Since this molecule is of great interest in connection with the spectrochemical investigations of diselenides, which are in progress at this institute by one of us³, we tried to dissolve it in the common spectroscopic solvents. It was, however, found to be quite insoluble at ordinary temperatures, but when heated to about 60° the yellow powder darkened and went into solution. This solution was yellow and showed an absorption maximum at about 4500 Å (Fig. 1). The colour persisted for several days at room temperature and then the yellow powder slowly precipitated. These facts indicate that the solution contains the monomer and that the yellow powder is a polymer, which depolymerizes when heated.

The corresponding sulphur compound (m. p. ca. 73°) prepared from trimethylenedibromide and sodium disulphide⁴ was also investigated. It dissolved without

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Received June 7, 1957.