weighed against the possibility of the presence of vitamin A₂ after reduction of our acetone extracts. The absorption maximum for the SbCl₅-reaction was at 700—720 mμ, compared with 693 mμ for vitamin A₄. We may, however, emphasize that very little is known with regard to all the possible isomers of vitamin A₄ and their spectrophotometric properties. The SbCl₅-colour of our "aldehyde"-fraction had a maximum slightly higher than that of the reduced compound.

The present investigation has thus confirmed the findings of Plack et al,¹ with regard to the presence of vitamin A₄ aldehyde in herring roe. We could not find vitamin A₄ aldehyde as reported by Pollard and Bieri.² The effect of the acetone treatment on vitamin A₄ aldehyde when the acetone-insoluble fraction of hexane extracts of herring roe was present, established a case where a natural product catalyses or takes part in the reaction between vitamin A₄ aldehyde and ketone-bodies. The reactions reported, when seen in relation to the chemical studies recorded ²⁴, suggest as a possible pathway for the formation in vivo of vitamin A₄, that it is derived from vitamin A₂ via the retinenes.


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Crystal Data of Nickel(II)dithiosemicarbazide-Sulphate

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K. A. Jensen¹ has described two forms of nickel(II)dithiosemicarbazide sulphate (Ni(Thio)₃SO₄) which he proposed to be cis-trans isomers.

As very few examples of stereoisomerism of nickel complexes have been definitely proved we have started an X-ray investigation in order to establish the complete structures of the two forms.

The α form crystallizes from water when mixing cold aqueous solutions of nickel sulphate and thiosemicarbazon. The product contains water of crystallization and the chemical analysis is consistent with the formula: Ni(Thio)₃SO₄·3H₂O. The water is removed by heating the product to 110°C and is slowly taken up again at room temperature.

Oscillation, rotation and Weissenberg diagrams were taken of crystals of Ni(Thio)₃SO₄·3H₂O using Cu-radiation.

The crystals are monoclinic with the following dimensions of the unit cell, unique axis b:

\[ a = 6.91 \text{ Å} \]
\[ b = 16.41 \text{ Å} \]
\[ c = 6.32 \text{ Å} \]
\[ β = 97.7 \]

The density of the crystal is approximately 1.84. Consequently there are two units of Ni(Thio)₃SO₄·3H₂O per unit cell.

The only systematic extinctions are h k 0 when k is odd. The possible space groups are \( P2_1/m \) and \( P2_2 \). A Patterson projection \( P(u, v) \) showed a large concentration of peaks at \( v = \frac{1}{2} \). No other line exhibited extraordinary concentrations of peaks. Hence the space group \( P2_2 \) is established.

The \( β \) form is precipitated from hot aqueous solutions of nickel sulphate and thiosemicarbazide. It contains no water of crystallization. Its powder diagram is different from that of the \( α \) form. It was

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rather difficult to obtain suitable crystals of the $\beta$ form for single crystal work and its space group has not yet been established. The solution of the structures will be pursued.


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Preliminary Note on the Configuration at C$_{22}$ of Solanum Alkaloids

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Tomatidine and 5a-solasonadanol-(3$\beta$) are generally believed to represent two types of Solanum alkaloids (aminoketal alkaloids) related to each other in the same manner as the "neo" and "iso" steroid sapogenins, i.e. they differ in configuration at C$_{22}$ by having an axial C$_{22}$-methyl group (structure II) and an equatorial C$_{22}$-methyl group (structure I), respectively.

Recently, Schreiber$^1$ and later Toldy$^2$ have suggested, however, that the two compounds differ in configuration at C$_{22}$. According to their formulation, tomatidine is a 22$\beta$-compound (structure III) and 5a-solasonadanol-(3$\beta$) a 22$\alpha$-compound (structure I). This difference in configuration at C$_{22}$ will cause the methyl groups at C$_{22}$ in both compounds to be equatorial.

The work submitted in this preliminary note supports the idea that tomatidine and 5a-solasonadanol-(3$\beta$) in fact differ in configuration at C$_{22}$. It was found that tomatidine forms an N-bromo as well as an N-chloro derivative, whereas 5a-solasonadanol-(3$\beta$) only forms an N-chloro derivative.

With the object of estimating the space requirements for binding a halogen atom to the nitrogen atom of ring F the hydrogen:halogen separation distances were measured on Dreiding molecular models. These measurements indicate that the distance between the N-halogen atom and two of the hydrogen atoms of the C$_{22}$-methyl group in structure I is 2.4 Å. In structure III the distance between the N-halogen and the hydrogen atom at C$_{22}$ is 2.6 Å.

Assigning a van der Waals radius of 1.0 Å to hydrogen and radii of chlorine and bromine of 1.8 Å and 1.95 Å, respectively, the distances H $\leftrightarrow$ Cl and H $\leftrightarrow$ Br can be estimated to 2.8 Å and 2.95 Å, respectively. Although the measured distances H $\leftrightarrow$ Hlg in structure I and III only are 2.4 Å and 2.6 Å, respectively, one can easily see, remembering the experimental facts, that the difference in the measured distances is of an order of magnitude allowing the formation of an N-chloro derivative, but not the formation of an N-bromo derivative in the case of 5a-solasonadanol-(3$\beta$). Furthermore, small distortions of the bond angles in rings E and F may increase the H $\leftrightarrow$ Hlg separation distances to values estimated using the van der Waals radii. Such distortions of bond angles are quite common.