

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 A₂. We may, however, emphasize that very little is known with regard to all the possible isomers of vitamin A₂ 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 A₁ aldehyde in herring roe. We could not find vitamin A₂ aldehyde as reported by Pollard and Bieri². The effect of the acetone treatment on vitamin A₁ aldehyde when the acetone-insoluble fraction of hexane extracts of herring roe was present, establishes a case where a natural product catalyses or takes part in the reaction between vitamin A₁ aldehyde and ketone-bodies. The reactions reported, when seen in relation to the chemical studies recorded³⁻⁵, suggest as a possible pathway for the formation *in vivo* of vitamin A₂, that it is derived from vitamin A₁ 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)₂SO₄), 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 *a* form crystallizes from water when mixing cold aqueous solutions of nickel sulphate and thiosemicarbazide. The product contains water of crystallization and the chemical analysis is consistent with the formula: Ni(ThiO)₂SO₄ · 3 H₂O. 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)₂SO₄ · 3 H₂O using Cu-radiation.

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

$$\begin{aligned} a &= 6.91 \text{ \AA} \\ b &= 16.41 \text{ \AA} \\ c &= 6.32 \text{ \AA} \\ \beta &= 97.7 \end{aligned}$$

The density of the crystal is approximately 1.84. Consequently there are two units of Ni(ThiO)₂SO₄ · 3H₂O per unit cell.

The only systematic extinctions are *h k 0* when *k* is odd. The possible space groups are *P2₁/m* and *P2₁*. 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 *P2₁* 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 *a* form. It was

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rather difficult to obtain suitable crystals of the β 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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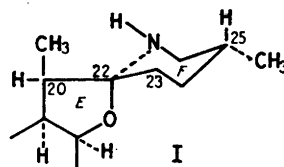
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Tomatidine and 5 α -solasodanol-(3 β) are generally believed to represent two types of *Solanum* alkaloids (aminoketal alkaloids) related to each other in the same manner as the "neo" and "iso" steroid sapogenins, *i. e.* they differ in configuration at C_{25} by having an axial C_{25} -methyl group (structure II) and an equatorial C_{25} -methyl group (structure I), respectively.

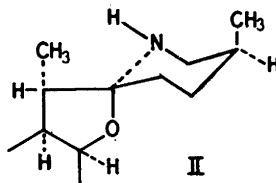
Recently, Schreiber¹ and later Toldy² have suggested, however, that the two compounds differ in configuration at C_{22} . According to their formulation, tomatidine is a 22 β -compound (structure III) and 5 α -solasodanol-(3 β) a 22 α -compound (structure I). This difference in configuration at C_{22} will cause the methyl groups at C_{25} in both compounds to be equatorial.

The work submitted in this preliminary note supports the idea that tomatidine and 5 α -solasodanol-(3 β) 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 5 α -solasodanol-(3 β) only forms an N-chloro derivative.

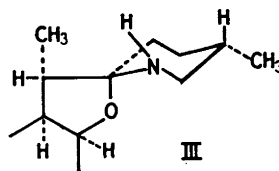
With the object of estimating the space requirements for binding a halogen atom to the nitrogen atom of ring F the hydrogen:halogen separation distances were measured on Dreiding molecular models. These measurements indicate that the distance between the N-halogen atom and two of the hydrogen atoms of the C_{20} -methyl group in structure I is 2.4 Å. In



22 α -iso



22 α -neo



22 β -iso

structure III the distance between the N-halogen and the hydrogen atom at C_{20} 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 5 α -solasodanol-(3 β). 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 common³.