wirklicht worden. Es gelang uns nun, von den genannten Lactamen ausgehend, in einem Reaktionsgang Hygrin, Cuskhygrin und Methylisopelletierin zu erhalten. Auch aus α-Piperidon konnten wir in analoger Reaktion Isopelletierin erhalten.

Nachdem damit die Gangbarkeit dieses Weges zur Synthese von Aminoaldehyden aus Lactamen erwiesen war, ließen wir in gleicher Weise $LiAlH_4$ auf 2-Oxooctahydroindolizin einwirken. Wir erhielten dabei eine unbeständige Verbindung, die nach ihren Eigenschaften, vor allem der Kondensationsfähigkeit mit Acetondicarbonsäure, den gesuchten 3-(α-Piperidyl)-propionaldehyd vorstellt. Die Derivate der Verbindung sind zum Teil ebenfalls instabil und entsprechen in ihren Eigenschaften nicht den in der Literatur beschriebenen Derivaten des Pelletierins.

Über die experimentellen Einzelheiten dieser Arbeit und die mit diesen Versuchen in Zusammenhang stehende Frage der Konstitution des Pelletierins erfolgen später ausführliche Veröffentlichungen in den Monatsheften für Chemie.

F. GALINOVSKY und R. WEISER

II. Chemisches Laboratorium der Universität Wien, den 24. März 1950.

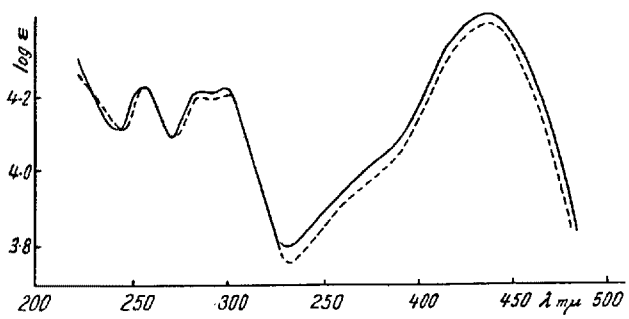
Summary

Whereas oxygen-free bases arise when an excess of $LiAlH_4$ acts on lactames, the corresponding aminoaldehydes, which serve as points of departure for the possible synthesis of alkaloids by the cells, are obtained when calculated quantities of $LiAlH_4$ are allowed to act on lactames. Through a corresponding reaction the not yet synthetically prepared 3-(α-Piperidyl)-propionaldehyde was formed from 2-oxooctahydroindolizine. Up to now the former has been assumed to be identical with the alkaloid of the pomegranate tree, pelletierine.

The Total Synthesis of *dl*-Rubremetinium Bromide

Confirmation of the structure of the alkaloid emetine[1] has been achieved by a synthesis of racemic O-methylpsychotrine (I) (mixed stereoisomers), identified by oxidation with mercuric acetate[2] to *dl*-rubremetinium bromide, having an absorption spectrum identical with that of *d*-rubremetinium bromide[1] derived from emetine.

Carbethoxyacetyl chloride was treated with β-3:4-dimethoxyphenylethylamine and the resulting amide, m. p. 63–64°, was cyclised with phosphoric oxide to ethyl 6:7-dimethoxy-3:4-dihydroisoquinoline-1-acetate (II), m. p. 85·5–86·5°. (Found: C, 64·9; H, 7·05; N, 5·20. $C_{15}H_{19}O_4N$ requires C, 64·9; H, 6·95; N, 5·05%.) Hydrogenation to the tetrahydroisoquinoline, m. p. 77–78°, was followed by treatment with ethyl α-formylbutyrate and hydrogenation of the crude condensation product, yielding the diester (III), m. p. 76–77°. (Found: C, 64·8; H, 8·43; N, 3·31. $C_{22}H_{33}O_6N$ requires C, 64·7; H, 8·15; N, 3·45%.) Dieckmann cyclisation followed by hydrolysis yielded the ketone (IV), m. p. 109–109·5°. (Found: C, 70·3; H, 7·8; N, 5·1. $C_{17}H_{23}O_3N$ requires C, 70·6; H, 8·0; N, 4·9%.) Reaction with ethyl cyanoacetate in the presence of ammonium acetate, followed by acid hydrolysis, decarboxylation, hydrogenation, isolation of the acidic product and esterification, gave the ester (V) (Found: N, 3·85. $C_{21}H_{31}O_4N$ requires N, 3·89%), which was heated with β-3:4-dimethoxyphenylethylamine at 180°. The resulting amide was cyclised with phosphoryl chloride, and the crude dihydroisoquinoline (I) was isolated from the basic products by distillation. From the products of its oxidation with mercuric acetate, *dl*-rubremetinium bromide was isolated as small, bright red needles, similar in appearance to authentic *d*-rubremetinium bromide, and melting with decomposition at 180–185°. (Found, after drying at 100°: N, 5·36. $C_{29}H_{33}O_4N_2Br$ requires N, 5·06%.)

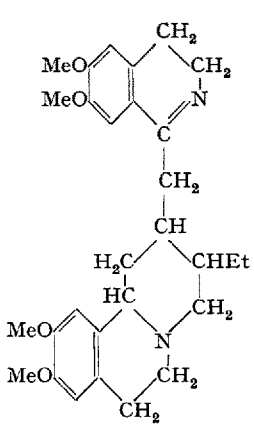


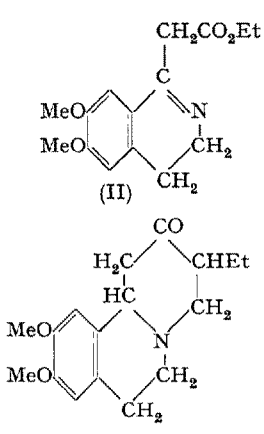
Absorption spectra in water
——— *d*-Rubremetinium bromide[3]
· · · · · · · · *dl*-Rubremetinium bromide, synthetic

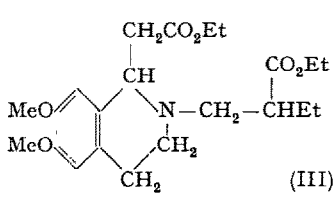
[1] A. R. BATTERSBY and H. T. OPENSHAW, Exper. *5*, 398 (1949); J. Chem. Soc. 3207 (1949). – M. PAILER and K. PORSCHINSKI, Mh. Chem. *80*, 94 (1949).

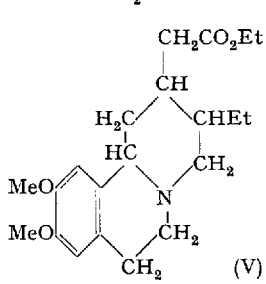
[2] A. R. BATTERSBY and H. T. OPENSHAW, J. Chem. Soc. 67 (1949).

[1] P. KARRER, C. H. EUGSTER, and O. RÜTTNER, Helv. chim. acta, *31*, 1219 (1948).


(I)


(II) (IV)


(III)


(V)

Full details of this synthesis will be published elsewhere. The work is being extended in various directions.

A. R. BATTERSBY and H. T. OPENSHAW

United College, University of St. Andrews, Scotland, September 5, 1950.

Zusammenfassung

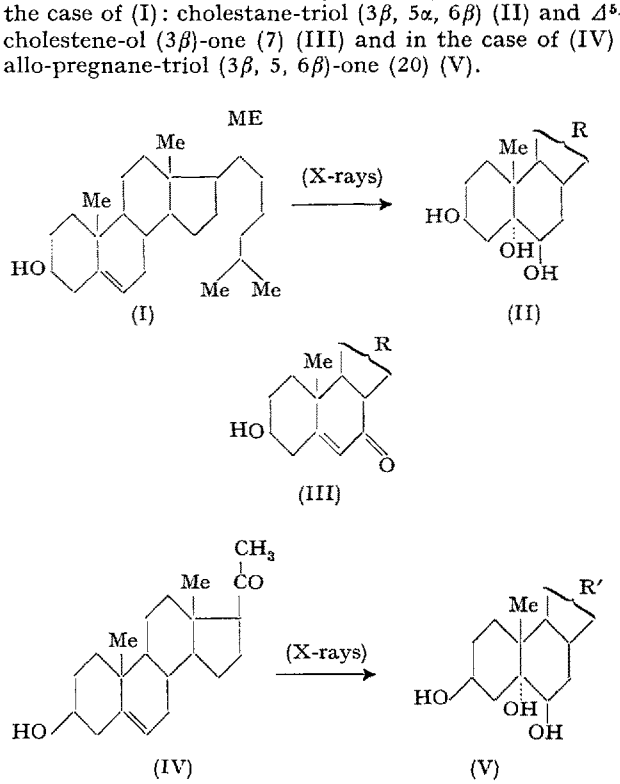
Die Verbindung (I) wurde über die Zwischenstufen (II)–(V) synthetisch aufgebaut. Die Oxydation von (I) mit Mercuriacetat lieferte *dl*-Rubremetiniumbromid, dessen Absorptionsspektrum mit demjenigen von *d*-Rubremetiniumbromid, dargestellt aus Emetin, identisch ist. Die heute als richtig angenommene Strukturformel von Emetin wird dadurch bestätigt.

Chemical Action of Ionizing Radiations on Steroid Compounds

Substances produced by the action of X-rays on cholesterol and on Δ^5-pregnene-ol-one in aqueous systems

In continuation of previous work[1] on the chemical action of ionizing radiations and the formation of free radicals and atoms in these processes[2] we have investigated the action of X-rays on cholesterol (I) and Δ^5-pregnene-ol-one (IV) in aqueous systems (aqueous solutions of water-soluble derivatives and aqueous acetic acid solutions).

From these irradiated solutions we were able to isolate and to characterize by unambiguous methods in the case of (I): cholestane-triol (3β, 5α, 6β) (II) and Δ^5-cholestene-ol (3β)-one (7) (III) and in the case of (IV): allo-pregnane-triol (3β, 5, 6β)-one (20) (V).



[1] G. STEIN and J. WEISS, Nature *161*, 650 (1948); *162*, 184 (1948). – F. T. FARMER, G. STEIN, and J. WEISS, J. Chem. Soc. (London) 3241 (1949). – G. STEIN and J. WEISS, J. Chem. Soc. (London) 3245, 3256 (1949). – H. LOEBL, G. STEIN, and J. WEISS, J. Chem. Soc. (London) 888 (1950).

[2] J. WEISS, Nature *153*, 748 (1944); Trans. Faraday Soc. *43*, 314 1947).

These substances are formed in good yields and we were always able to account for 80 and sometimes 90% of the starting materials.

It is worth noting that compound (II) has been isolated from the arterio-sclerotic human aorta[1], from pig's testes[2], and from beef liver[3], and compound (III) from bull's testes[4] and from pig's testes[5].

The results obtained may be of some general interest on account of the importance of sterols and steroid hormones in cell metabolism and in view of the role of cholesterol as a precursor in the bio-synthesis of steroid hormones and the close relationship of Δ^5-pregnene-ol-one to the sex hormones.

A full account including a discussion of the mechanism of these processes will be published elsewhere.

This work was supported by a grant from the Medical Research Council to whom our thanks are due.

JOSEPH WEISS and MAX KELLER

University of Durham, King's College, Newcastle on Tyne, England, May 12, 1950.

Zusammenfassung

Nach der Bestrahlung verdünnter Lösungen von Cholesterin beziehungsweise Δ^5-Pregnen-ol-(3β)-on-(20) mit Röntgenstrahlen, isolierten wir Cholestan-triol-(3β, 5α, 6β) und Δ^5-Cholesten-ol-(3β)-on-(7) beziehungsweise allo-Pregnan-triol-(3β, 5, 6β)-on-(20).

[1] E. HARDEGGER, L. RUZICKA, and E. TAGMANN, Helv. chim. acta *26*, 2205 (1943).

[2] L. RUZICKA and V. PRELOG, ib. *26*, 975 (1943).

[3] G. A. D. HASLEWOOD, Biochem. J. *35*, 708 (1941).

[4] F. STEINMANN, Helv. chim. acta *26*, 2222 (1943).

[5] V. PRELOG, E. TAGMANN, S. LIEBERMANN, and L. RUZICKA, ib. *30*, 1080 (1947).

The Structure of $NaPt_3O_4$

Following JÖRGENSEN[1] and WÖHLER[2] we have prepared a platinum oxide by heating an intimate mixture of sodium chloroplatinate and sodium carbonate just to melting. JÖRGENSEN's analysis of the product led him to the formula Pt_3O_4 while WÖHLER's more detailed analysis gave varying results fitting a formula PtO_x with $1 \leqq x \leqq 2$. WÖHLER found that the product also contained small amounts of water and sodium which could not be removed even by boiling with acids. The work reported here shows that the compound formed is actually $NaPt_3O_4$.

X-ray powder diagrams of our jet black preparation showed a set of very sharp lines which could be indexed on a cubic simple lattice of cell edge $5{\cdot}689 \pm 0{\cdot}002$ Å. Accurate intensity values for filtered CuK_α radiation were obtained for $\vartheta < 45°$ with a Norelco Geigerconteur instrument and for higher values of ϑ by careful visual analysis using the multiple film technique and applying an absorption correction.

Systematic extinctions led to the probable space groups $O_h^3 - Pm3n$ and $T_d^4 - P\bar{4}3n$. It was further found that reflections (*hkl*) occured only when either of the following conditions was satisfied:

$$h + k + l = 2n; \quad (1)$$

$$h = 4n,\ k = 4n + 2,\ l = 4n \pm 1. \quad (2)$$

[1] S. M. JÖRGENSEN, J. pr. Chem. *16*, 344 (1877).

[2] L. WÖHLER, Z. anorg. Chemie *40*, 450 (1904).