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

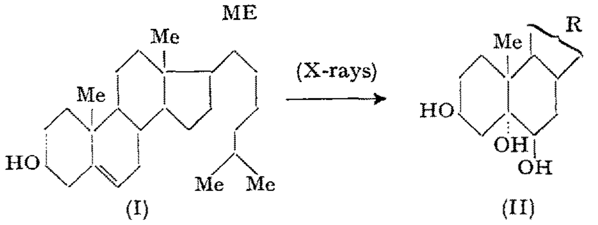
Die Verbindung (I) wurde über die Zwischenstufen (II)-(V) synthetisch aufgebaut. Die Oxydation von (I) mit Mercuriacetat lieferte *dl*-Rubremetiniumbromid, dessen Absorptionsspektrum mit demjenigen von *d*-Rubremetiniumbromid, dargestellt aus Emetin, identisch ist. Die heute als richtig angenommene Strukturformel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

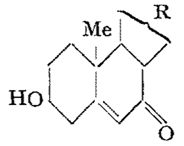
Chemical Action of Ionizing Radiations on Steroid Compounds

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

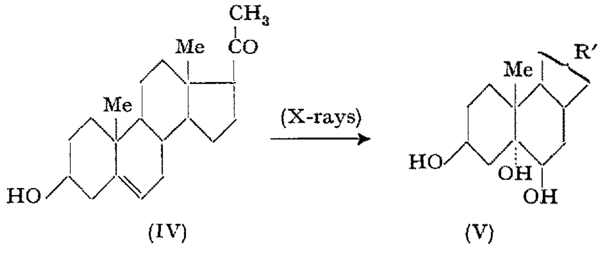
In continuation of previous work[1] on the chemical action of ionizing radiations and the formation of free radicals and atoms in these processes[2] we have investigated the action of X-rays on cholesterol (I) and Δ^5-pregnene-ol-one (IV) in aqueous systems (aqueous solutions of water-soluble derivatives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





(III)



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).

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

[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:

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

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

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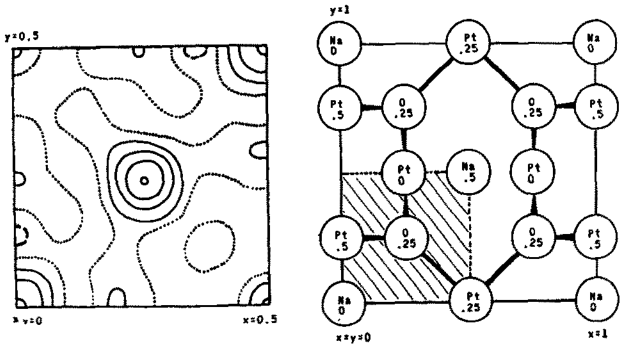
[1] S. M. Jörgensen, J. pr. Chem. *16*, 344 (1877).

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

The only positions that are compatible with these special extinction rules are the two equivalent sets of 6-fold positions 6*c* and 6*d*[1] in O_h^3 or T_d^4. One of these sets, e. g. 6*c*, $\pm$ ($\frac{1}{4}$ O $\frac{1}{2}$, $\nearrow$) [2], must therefore be occupied by six Pt-atoms. Two more Pt-atoms might be placed at the origin and the cube center (positions 2a) but then ten actually observed lines should be absent or very weak. There is fair agreement between observed and calculated intensities at this stage.

Even with heavy exposures, no additional lines could be discovered. The scattering from the remaining atoms should therefore fulfill either of the above extinction rules (1) and (2), or both. Condition (2) (together with [1]) is satisfied only by the sets 6*c* and 6*d* discussed above (the former filled with Pt-atoms and the latter not available because of space requirements), but condition (1) alone is precisely that for a body centered lattice. The remaining atoms are thus arranged on a body centered lattice. This and spatial considerations lead to the alternative of positions 8*e* of O_h^3 or the related positions 8*e* of T_d^4 for the O-atoms.



1 *a* 1 *b*

Fig. 1*a*. – Projection ϱ' (x, y) on (001)-plane. Contours in arbitrary units, zero contour dotted, negative contour dashed.

Fig. 1*b*. – View of unit cell along *c*-axis. Numbers are *z*-parameters, with the additional stipulation that the value 0·25 indicates an atom at $z = 0{\cdot}25$ as well as at $z = 0{\cdot}75$.

A Fourier projection ϱ' (x, y) with Pt-atoms removed was prepared using as coefficients the algebraic differences between the observed structure factors (with signs deduced from the Pt-contributions) and calculated structure factors based on the Pt-scattering only. In the case that several forms reflected at an equal ϑ-value, the total intensity was divided among the components of the line proportionally to the frequency factors.

Fig. 1*a* shows one quarter of the unit cell of this projection. The peak at the center of the diagram contains two superimposed O-atoms and thus fixes the oxygen parameters at positions 8*e* of O_h^3, (000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) + ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{3}{4}\frac{3}{4}$, $\nearrow$). The peak at the origin shows the presence of sodium in the crystal, its magnitude amounting to roughly 70% of the oxygen peak (expected about $\frac{10}{16} \approx 0{\cdot}6$ for $\left.\frac{\text{Na}^+}{2\text{O (superimposed)}}\right)$. There are then Na-ions inside the cubes formed by the O-atoms, two per unit cell, filling the positions 2*a* of O_h^3 with parameters (000, $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$). The possibility exists that some of these oxygen cubes remain unfilled but the magnitude of the sodium peaks suggests that this is not the case in our substance. The projection shows some other much smaller peaks which are probably due to incomplete subtraction of the Pt-contributions, experimental inaccuracies of observed intensities, breaking-off error, and incorrect apportioning of intensities to components of lines in which several reflections superimpose. The agreement between observed and calculated intensities is excellent if the oxygen and sodium contributions are included. Fig. 1*b* is a view of the complete unit cell along the *c*-axis and indicates the portion shown by the Fourier projection of Fig. 1*a*.

The formula of the oxide under discussion is thus found to be $NaPt_3O_4$. This explains the presence of sodium in WÖHLER's analysis. The varying amounts of oxygen found by WÖHLER could be explained by the assumption of the additional presence of amorphous platinum oxides to which might be adsorbed the water found by him. The space group of the structure is O_h^3–Pm3*n*. All Pt-atoms are equivalent and have thus the oxidation number $\frac{7}{3}$. The coordination and bonding of the various atoms can be described as follows (cf. Fig. 1*b*). Each sodium is surrounded by eight oxygens at the corners of a cube at a distance of 2·463 Å. Each oxygen is in the center of a symmetrical trigonal bipyramid the apices of which are formed by two Na-ions at 2·463 Å and the central triangle by three O-atoms at 2·011 Å. Each platinum is surrounded octahedrally, being in the middle of a square of four O-atoms at 2·011 Å and joined above and below to two Pt-atoms at 2·845 Å. The Pt-O distance is within 0·01 Å of the Pt-O distance found in Pt-O[1] (2·02 Å) and thus corresponds essentially to a single bond between platinum and oxygen. These bonds are shown in Fig. 1*b*. The Pt-Pt distance is close enough for covalent bonding of these metal atoms (these bonds are not shown in Fig. 1*b*), the value of the bond number[2] being 0·377. The sodium oxygen bonding is essentially of ionic character. The sum of the ionic radius[3] of Na^+ (0·95 Å) and the van der Waal's radius[3] of O (1·40 Å [ionic radius 1·32 Å]) is 2·35 Å so that the Na-ion fit very loosely inside the oxygen cubes.

The presence of infinite strings of bonded Pt-atoms parallel to the cubic axes implied possible metallic conduction in $NaPt_3O_4$. It turned out, however, that conduction occurs essentially by an ionic mechanism, probably involving the Na-ions. The specific resistance is of the order of 10^4 ohm-cm at room temperature.

A full report of this work is to be given elsewhere.

JÜRG WASER and EDWIN D. MCCLANAHAN, jr.

Chemistry Department, The Rice Institute, Houston, Texas, June 18, 1950.

Zusammenfassung

Eine mikrokristalline Platinverbindung der Formel $NaPt_3O_4$ wird beschrieben. Alle Platinatome sind gleichwertig und die Koordinationen sind die folgenden: Platin 4O und 2Pt; Sauerstoff: 3Pt und 2Na; Natrium: 8O. Die Substanz ist ein ionischer Leiter.

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[1] *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Berlin 1935, vol. 1.

[3] The symbol $\nearrow$ stands for cyclical permutation.

[1] W. J. MOORE, jr., and L. PAULING, JACS *63*, 1392 (1941).

[2] L. PAULING, JACS *69*, 542 (1947).

[3] L. PAULING, *The Nature of the Chemical Bond* (Ithaca, 1939).