C 59·34, H 6·30). The des-base, on distillation with zinc dust, yields 1,2,3,4-tetrahydrophenanthrene, isolated as its picrate, m. p. 108–110°, not depressed by admixture with authentic 1,2,3,4-tetrahydrophenanthrene picrate, and further characterized as its trinitrobenzene derivative, m. p. 126·5–127·5°, not depressed by admixture with authentic 1,2,3,4-tetrahydrophenanthrene-trinitrobenzene of m. p. 128–129°, (Calc.: C 60·75, H 4·34; Fd.: C 60·67, H 4·96).

If our supposition as to the point of attachment of the nitrogen atom (at C 9) is correct, then the isomerism[1] of our base and GREWE'S morphinane must be the result of isomerism at carbon atoms 13 and 14. Degradative work designed to ascertain the stereochemical nature of the ring juncture in question has been begun in this laboratory.

The 3,4-dimethoxy derivative of I (m. p. 238–239°, Calc.: C 69·44, H 5·51; Fd.: C 69·77, H 5·65) has also been prepared in quantity, and its reduction is under investigation.

M. GATES and W. F. NEWHALL

Park Laboratory, Bryn Mawr College, Bryn Mawr, Pa., January 10, 1949.

Zusammenfassung

9,10-Dioxo-13-cyanmethyl-5,8,9,10,13,14-hexahydro phenanthren wurde durch eine Reihe von Reduktionen, deren Mechanismus nicht vollständig aufgeklärt ist, in eine neue Verbindung übergeführt. Diese besitzt sehr wahrscheinlich das Kohlenstoff/Stickstoffgerüst des Morphins oder eines seiner Stereoisomeren. Es wird über Abbaureaktionen berichtet, die diese Struktur bestätigen können.

[1] Prof. R. GREWE has informed us privately that a by-product of his synthesis, obtained in small amounts[2] appears to be identical with our substance (correspondence in melting points of picrate, methiodide, desbase picrate, dihydrodesbase picrate).

[2] Concerning *Pikrat A* vide R. GREWE, Ber. Dtsch. chem. Ges. *81*, 285 (1948).

Some Observations on the Oxidative Degradation of Cholesterol

The oxidation of cholesterol acetatedibromide with chromic acid, as developed by RUZICKA[1], is now classic. From the breaking-down of the aliphatic side-chain of cholesterol by this method a variety of degradation products results, such as dehydroisoandrosterone, pregnenolone, etiocholenic acid, etc.[2], which are important in the synthesis of biologically active steroids. 5-Dehydroisoandrosterone is frequently used as starting material for such syntheses. The mechanism of this oxidative degradation is incompletely understood. Recently BILLETER and MIESCHER[3] advanced a theory on the side-chain fission of cholesterol with chromic acid. They assume that the tertiary carbon-atoms at C_{14}, C_{17}, C_{20}, and C_{25} are the points where the molecule is attacked and from which directly, or indirectly from other intermediate products, tertiary carbinols arise. When split off, these hydroxy groups would yield water while the resulting carbon-carbon double bonds are then disrupted, giving rise to ketones and acids. Many compounds have been isolated and identified that afford confirmation of this theory[2].

[1] L. RUZICKA, Swiss Pat. 182391 (1933). – L. RUZICKA and A. WETTSTEIN, Helv. chim. acta *18*, 987 (1935).

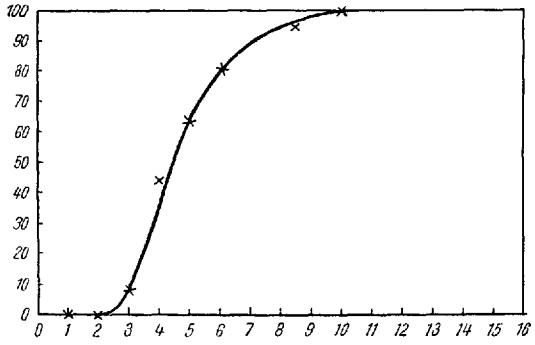
[2] For a review see: J. R. BILLETER and K. MIESCHER, Helv. chim. acta *30*, 1415 (1947).

[3] J. R. BILLETER and K. MIESCHER, Helv. chim. acta *30*, 1414 (1947).

As in this laboratory a similar conclusion as to "intermediate products" had been drawn from other experiments, it was decided to present a few relevant results.

The rate of formation of dehydroisoandrosterone acetate from cholesterol acetatedibromide by oxidation with chromic acid in a solution of glacial acetic acid and dichlorethane was determined. For this purpose the dehydroisoandrosterone acetate formed had to be estimated at various stages of the reaction.

In view of the quantitatively inaccurate and laborious methods available, the isolation of this ketone from the other ketones known to be produced by the oxidation was avoided. Instead of this the colorimetric assay of 17-ketosteroids with the reaction of ZIMMERMANN[1], as adapted by CALLOW and coworkers[2], was used. In this assay advantage is taken of the instability of the coloured reaction products of the 20-, 25-, and other keto-steroids with m-dinitrobenzene in alkaline alcoholic solution, in contradistinction to the more lasting colour



The figure shows the amounts of 5-dehydroisoandrosterone acetate (I), formed by oxidation of cholesterol (as its acetate dibromide) with chromic acid, against time. – The reaction time (in hours) is plotted on the abscissa. The ordinate represents the amounts of (I) expressed in percentage of the total dehydroisoandrosterone acetate formed.

obtained with 17-keto-steroids, e. g., dehydroisoandrosterone acetate. Thus, for instance, the oxidation products of cholesterol, $\Delta^{5,6}$-pregnene-ol-(3β)-acetate-one-20 and $\Delta^{5,6}$-nor-cholestene-ol-(3β)-acetate-one-25 give labile coloured products with colour values of about $^1/_8$ and $^1/_{10}$ respectively of that of dehydroisoandrosterone acetate. These are known to be formed in much smaller amounts than dehydroisoandrosterone acetate. The other known oxidation products gave such faint colours as to be also negligible. The oxidations were performed approximately by the usual procedure[3], using glacial acetic acid distilled over chromic acid and dichlorethane with a negligible chromic acid titre. The reaction temperature was kept constant within $\pm$ 2°. The chromic acid solution was added at a uniform rate over 7 hours and the consumption of the oxidant was controlled iodometrically. At regular intervals aliquot samples were taken and the mixture of reaction components in the samples was "fixed" by reduction of the small excess of chromic acid with methanol. The samples were further worked up by evaporating the dichlorethane *in vacuo*, splitting off the bromine with zinc dust and

[1] W. ZIMMERMANN, Z. physiol. Ch. *233*, 257 (1935); Vitamine und Hormone *5*, 1 (1944); Schweiz. med. Wschr. *76*, 805 (1947).

[2] N. H. CALLOW, R. K. CALLOW, and C. W. EMMENS, Biochem. J. *32*, 1312 (1938).

[3] For experimental details see F.I.A.T. Final Report No. 996. ed. by C. R. ADDINALL, p. 29 (London, 1947).

separating the debrominated reaction mixtures into acid and neutral components.

The neutral components were dissolved in ether in a stoppered graduated flask and, after a preliminary colorimetric assay, dilutions were made containing about 100–150 μg dehydroisoandrosterone acetate p. ml. From each of these solutions 6 samples of 1 ml were taken and the average of the colorimetric values was read on a daily standard curve[1].

The relation between the formation of dehydroisoandrosterone acetate (in percentage of total dehydroisoandrosterone acetate formed) and reaction time (in hours) is shown graphically in the Figure.

Iodometric determinations of chromic acid showed that the chromic acid consumption started at once and that, in the early stages of the reaction at least, the chromic acid was consumed approximately as fast as it was added; towards the end of the reaction the consumption decreased. From the Figure it is evident that, although the chromic acid was readily consumed in the beginning, the formation of dehydroisoandrosterone acetate began later, then proceeding rapidly and diminishing only when the starting material was used up. In the initial period such small amounts of acids were formed that they could not account for the chromic acid consumption. These facts suggest that dehydroisoandrosterone acetate is formed by a secondary reaction, subsequent to other chromic-acid-consuming reactions, as was theoretically inferred[2].

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Pharmaco-therapeutic Laboratory of the Municipal University, Amsterdam, and Research Laboratory of Organon Ltd., Oss, Netherlands, January 9, 1949.

Résumé

La vitesse de formation de déhydroïsoandrostérone-acétate (I) provenant de cholestérol-acétatedibromide par l'oxydation avec de l'acide chromique est soumise a un examen. Les quantités produites de I sont déterminées à l'aide de la réaction colorimétrique de ZIMMERMANN. Le rapport, entre les teneurs de I et la durée de la réaction, est reproduit graphiquement. Il s'en déduit l'existence d'une période d'induction qui s'explique par une réaction précédant la formation de I et produisant des matières intermédiaires. Cette conclusion est conforme à une hypothèse récente, basée sur d'autres considérations.

[1] A. Klett-Summerson photo-electric colorimeter with filter No. 54 was used; Klett Mfg. Co., New York; W. H. SUMMERSON, J. Biol. Chem. *130*, 149 (1939).

[2] J. R. BILLETER and K. MIESCHER, Helv. chim. acta *30*, 1414 (1947).

Expression allométrique de la précocité d'un légume-racine *(Daucus)*

Nous avons consacré un récent mémoire[1] à la définition des variétés de carottes potagères et fourragères. Ces essais de «typisation», préliminaires indispensables des opérations de sélection et d'hybridation, faisaient appel aux caractères de forme et de longueur de la racine. La diagnose d'un légume-racine comporte encore d'autres éléments. Parmi eux, le feuillage joue un rôle important. La présente note s'y rapporte et précise les proportions existant entre les appareils aérien et souterrain.

L'importance du feuillage diffère beaucoup d'une variété de carotte à l'autre et détermine certains modes de culture: plein-champ, maraîcher, etc. Les praticiens sélectionnent enfin, pour la culture hâtive sous châssis, des types à feuillage réduit. Un reclassement de ces notions familières aux cultivateurs est indispensable aux recherches génétiques. Etablissons donc l'indice de feuillage, I_f, soit le rapport du poids des feuilles au poids de la plante. On pèse à cet effet 100 plantes fraîchement déracinées; le feuillage est aussitôt coupé au ras du collet, puis pesé. Cette mesure est effectuée au moment de l'arrachage, c.-à-d. quand les racines sont mûres et n'augmentent pour ainsi dire plus de poids. Il s'agit donc d'un moment facilement déterminable de la période végétative. L'aspect évolutif du problème sera considéré plus loin. Voici les résultats obtenus en 1946 avec diverses variétés cultivées dans des conditions comparables (voir colonne 1 du tableau):

Variétés	I_f	e	I_p
Amsterdam	0,12	7,3	—
Vertou	0,12	7,3	—
Nantaise	0,14	6,1	74
des Halles	0,15	5,7	63
Nantaise-Touchon	0,15	5,7	70
Grelot	0,19	4,3	—
Berlicum	0,21	3,8	—
Duwicker	0,22	3,5	85
Chantenay	0,22	3,5	—
de Meaux	0,25	3,0	—
Parisienne	0,27	2,7	71
Jaune du Doubs	0,28	2,6	—
Guérande	0,29	2,4	80
Flackker	0,32	2,1	—
St-Valéry	0,35	1,8	90
Blanche à collet vert	0,40	1,5	—

I_f indice feuillage, e quotient d'économie
I_p indice de précocité, fixé par l'âge en jours atteint au point d'inversion (voir le texte)

La gamme est continue des feuillages les plus légers, auxquels ne sont pas nécessairement liées les racines les plus courtes, jusqu'aux feuillages les plus lourds. Ces valeurs s'ajoutent aux autres caractéristiques raciales. Si les plantes soumises aux mesures sont des génotypes faiblement hétérozygotiques, les indices obtenus resteront significatifs pour chaque lignée dans des conditions d'autogamie.

Il faut s'attendre d'autre part, à ce que ces valeurs soient déformées pour un même lot de graines semées plusieurs années de suite ou développées dans des conditions culturales différentes au cours d'une même saison. Ces aberrations, dont la phénogénétique rend compte, seront à leur tour mesurées.

Quotient d'économie: e. — Chez la carotte, le feuillage n'a d'intérêt qu'en fonction des racines. Le rapport $R/F = \frac{poids\ de\ la\ racine}{poids\ du\ feuillage} = e$, exprimera dorénavant le poids de racine produite par un kilogramme de feuillage. Cette valeur mesure la puissance constructrice de l'unité

[1] F. CHODAT et FR. GAGNEBIN, Arch. Jul.-Klaus-Stiftung, *23* (1948).