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Organisch-chemische Anstalt der Universität Basel, den 28. April 1951.

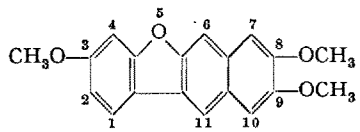
Summary

The isomerisation of 5-hydroxy-benz(cd)indoline (I) to 5-keto-1,3,4,5-tetrahydro-benz(cd)indole (II) over a palladium catalyst has been studied systematically. Besides (II) varying amounts of the dehydrogenation product (III) are formed. This side reaction does not occur when the isomerisation is carried out in a hydrogen atmosphere.

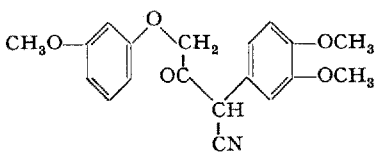
The above isomerisation can be reversed by treatment of (II) with acetanhydride and potassium acetate.

A Synthesis of Kostanecki's 3:8:9-Trimethoxy-β-brazan

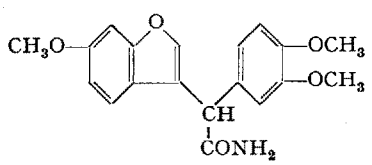
By heating trimethylbrazilone with hydriodic acid for a long period, KOSTANECKI and LLOYD[1] obtained 3:8:9-trihydroxy-β-brazan which gave the trimethyl ether (I, m. p. 244–246°C) on methylation. The constitution of (I) was confirmed by converting the above-mentioned hydroxybrazan to β-brazan with the aid of zinc dust. The compound (I) has now been synthesised by an unambiguous method.



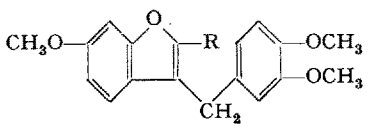
(I)



(II)



(III)



(IV)

The keto-nitrile (II) of PFEIFFER *et al.*[2] gave, on treatment with fuming hydrochloric acid in acetic acid at 30°C, the isomeric amide (III, m. p. 162°C). This on prolonged boiling with 10% hydrochloric acid afforded 6-methoxy-3-(3:4-dimethoxybenzyl)-coumarone (IV, R = H, m. p. 61–62°C; picrate, m. p. 102°C). On Gattermann synthesis with the aid of zinc chloride IV (R = H) gave 6-methoxy-3-(3:4-dimethoxybenzyl)-2-formylcoumarone (IV, R = CHO, m. p. 137°C; 2:4-dinitrophenylhydrazone, m. p. 246–248°C), the orientation of which was established by oxidising it with potassium permanganate in acetone to the known acid[1] (IV, $R = CO_2H$, m. p. 196°C). The aldehyde (IV, R = CHO) underwent quantitative cyclodehydration[2] to I (m. p. 244–246°C) with glacial phosphoric acid at 100°C. The correctness of the synthesis was confirmed by typical colour reactions[3] and oxidising (I) with chromic acid to trimethoxy-β-brazanquinone (m. p. 261–262°C)[4] which was purified by sublimation in vacuum.

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Résumé

Une manière non équivoque de synthèse de 3,8,9-triméthoxy-β-brazan de KOSTANECKI se décrit dans cet article.

[1] V. KOSTANECKI and L. LLOYD, Ber. Dtsch. chem. Ges. *36*, 2198 (1903).

[2] P. PFEIFFER, K. QUEHL, and F. TAPPERMANN, Ber. Dtsch. chem. Ges. *63*, 1304 (1930).

[1] K. W. BENTLEY and R. ROBINSON, J. Chem. Soc. 1950, 1355.

[2] C. K. BRADSHER, Chem. Rev. *38*, 492 (1946).

[3] V. KOSTANECKI and L. LLOYD, Ber. Dtsch. chem. Ges. *36*, 2198 (1903).

[4] V. KOSTANECKI and L. LLOYD, Ber. Dtsch. chem. Ges. *36*, 2200 (1903).

7-Oxo-dehydro-iso-androsterone Acetate

During the purification of technical dehydro-iso-androsterone acetate by crystallization from methanol, the final mother-liquor showed no tendency to crystallization. The residue was dissolved in benzene and this solution subjected to chromatography over Al_2O_3. Elution also took place with benzene.

The first fractions contained crystals which could not be identified. From the intermediate fractions crystals have been isolated with a melting range from 160–170°. By recrystallization first from methanol and subsequently from 40% aqueous methanol, the m. p. could be raised to 176–178°. The analysis yielded the following results: C: 73·21 and 73·15%, H: 8·40 and 8·33%. The values, calculated for an oxo-dehydro-iso-androsterone acetate are: C: 73·12%, H: 8·19%. A mixed m. p. with 7-oxo-dehydro-iso-androsterone acetate prepared according to BILLETER and MIESCHER[1] gave no depression. The U. V. absorption spectrum showed a maximum at 235 mμ with a log ε of 4·09. A similar maximum is observed in the spectrum of 7-oxo-cholesterol acetate.

The isolation of 7-oxo-dehydro-iso-androsterone acetate from the oxidation products of cholesterol has not yet been described. BILLETER and MIESCHER[2] isolated Δ-3,5-androstadienedione-7,17 from the mother-liquors of the dehydro-iso-androsterone semicarbazone and it is not unlikely that this compound has been formed from 7-oxo-dehydro-iso-androsterone acetate during the purification process.

[1] J. R. BILLETER and K. MIESCHER, Helv. chim. acta *31*, 629 (1948).

BILLETER and MIESCHER[1] proposed a scheme to account for the oxidation products of cholesterol acetate dibromide. They assume that in the first place tertiary C-atoms are attacked by oxygen, thus yielding tertiary alcohols. These points are liable to further oxidations.

With the aid of these assumptions it is possible to explain the formation of the oxidation products isolated so far. All these substances are formed by the destruction of the side-chain or by the oxidation of ring D.

As yet, only one compound, Δ-3,5-androstadiene-dione-7,17 (see above), where oxidation had occurred in ring B, had been isolated.

The formation of 7-oxo-dehydro-iso-androsterone acetate may be explained by the presence of unbrominated cholesterol acetate, which usually occurs in the starting material. This contamination will be oxidized at C 7.

Other 5,6 unsaturated steroids as well yield 7-oxo-compounds on oxidation, for instance cholesterol acetate to 7-oxo-cholesterol acetate (WINDAUS, LETTRÉ and SCHENCK[2]).

The 7-oxo-cholesterol acetate on further oxidation will lose the side-chain to give 7-oxo-dehydro-iso-androsterone acetate.

Little can be said about the amount of this compound formed during the oxidation of dibromo-cholesterol acetate, but it will depend on the completeness of the bromination and thus widely vary.

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Research Laboratories, N. V. Organon, Oss, Holland, April 24, 1951.

Zusammenfassung

Bei der Reinigung von technischem Trans-Dehydro-androsteronazetat gelang es, durch Chromatographie der letzten Mutterlaugen Δ 5-3β-azetoxy-androsten-dion-(7,17) zu isolieren. Diese Verbindung war bisher in den Oxydationsprodukten des Cholesterinazetatdibromids noch nicht gefunden worden. Wahrscheinlich ist sie bei der Oxydation von nicht bromiertem Cholesterolazetat entstanden.

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

[2] A. WINDAUS, H. LETTRÉ, and FR. SCHENCK, Ann. Chem. *520*, 98 (1935).

The Nomenclature of the Spinochromes of Sea Urchins

The name echinochrome was coined in 1885 by MACMUNN[1] to designate the red pigment of the elaeocytes of sea urchin. The name spinochrome was given in 1938 by LEDERER and GLASER[2] for a similar darker pigment found in the spines of the sea urchin, *Paracentrotus lividus*. In 1939 KUHN and WALLENFELS[3] proposed to add suffixes to echinochrome and spinochrome to distinguish the various pigments found in the eggs and spines of different species. The pigment isolated from *Arbacia pustolusa* eggs was called echinochrome *A* and that from *Paracentrotus lividus* spines called spinochrome *P*. On the evidence available in 1940, LEDERER[4] did not consider that this addition of suffixes was warranted; however later in 1940, KUHN and WALLENFELS[1] isolated, in small amounts, further echinochromes, *B* and *C*, from *Arbacia* eggs and in 1942 MUSAJO and MINCHILLI[2] isolated spinochrome P_1 from *Paracentrotus* spines. GOODWIN and SRISUKH[3], in 1950 attempted to standardize the nomenclature by suggesting that KUHN and WALLENFELS[4] scheme regarding echinochromes be adopted but that the spinochromes should be renamed spinochrome *A*, *B*, etc., instead of *P* and P_1; *P* and P_1 were used originally to indicate the origin of the pigment (*Paracentrotus*)[5], but as these also occur in other species (e. g. *Echinus esculentus*) it was concluded that ambiguity would be avoided if these prefixes were dropped and *A*, *B*, *C*, etc., substituted.

The principle of the nomenclature suggested by GOODWIN and SRISUKH[3] is acceptable, but, as will be pointed out later, the details will have to be altered somewhat in the light of recent work. There does arise, however, a more important point as to whether the separate terms spinochrome and echinochrome are justified, because the work of LEDERER and GLASER[6] recently repeated by LEDERER[7], and confirmed in the Liverpool laboratory, indicated that echinochrome *A* is not confined to the eggs and (or) perivisceral fluid of urchins, but also occurs in the test and spines. We feel that the differentiation is still valid for two main reasons (*a*) spinochromes have not as yet been observed in eggs or perivisceral fluid, (*b*) that LEDERER[7] has observed that the organic residue remaining after dissolution of the spines and test of *Paracentrotus* in HCl, contains both echinochrome *A* and spinochrome *A*, but in this case the echinochrome *A* is the major component. This organic residue, consisting of the bases and motor muscles of the spines, can quite reasonably be considered as the site of conversion of the echinochrome into spinochrome prior to the latter's incorporation into the calcified regions. It is possible then that the echinochrome found in spines comes from small amounts of organic residue (which would be extremely difficult to dissect out) and does not in fact occur in the calcified regions; it is also possible that both spinochrome and echinochrome are transferred to these regions (cf. MOORE[8]). In any case, whatever is the final explanation there is no reasonable doubt that the spinochromes are specifically incorporated into the test and spines, and thus one is justified in maintaining the distinction between spinochromes and echinochromes.

We therefore propose that the following nomenclature be adopted (Table) for spinochromes; further pigments when isolated could then be added to this list by adding the appropriate letter to spinochrome.

Apart from the inclusion of new pigments[9] this scheme differs from that of GOODWIN and SRISUKH[3] in two major details. Isoechinochrome, the occurence of which

[1] C. A. MACMUNN, Quart. J. Micr. Sci. *25*, 469 (1885).

[2] E. LEDERER and R. GLASER, C. r. Acad. Sci. Paris *207*, 454 (1938).

[3] R. KUHN and K. WALLENFELS, Ber. Dtsch. chem. Ges. *72*, 1407 (1939).

[4] E. LEDERER, Biol. Rev. *15*, 273 (1940).

[1] R. KUHN and K. WALLENFELS, Ber. Dtsch. chem. Ges. *73*, 458 (1940).

[2] L. MUSAJO and M. MINCHILLI, Bol. sci. Fac. Chim. Ind. Bologna *3*, 113 (1942).

[3] T. W. GOODWIN and S. SRISUKH, Biochem. J. *47*, 69 (1950).

[4] R. KUHN and K. WALLENFELS, Ber. Dtsch. chem. Ges. *72*, 1407 (1939).

[5] L. MUSAJO and M. MINCHILLI, Bol. sci. Fac. Chim. Ind. Bologna *3*, 113 (1942); Gazz. Chim. Ital. *70*, 287 (1940).

[6] R. GLASER and E. LEDERER, C. r. Acad. Sci. Paris *208*, 1939 (1939).

[7] E. LEDERER, Biochim. biophys. acta (1951) (in press).

[8] H. B. MOORE, J. Mar. biol. Ass. U. K. *21*, 711 (1937).

[9] E. LEDERER, Biochim. biophys. acta (1951) (in press).