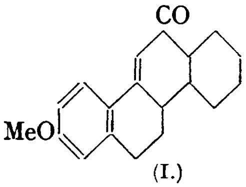
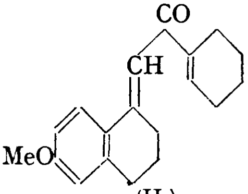
173. *Experiments on the Synthesis of Substances Related to the Sterols. Part XI. The Constitution of the Condensation Products from Acetyl*cyclo*pentene or Acetyl*cyclo*hexene and Methoxytetralone.*

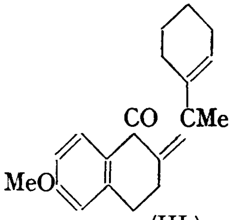
By (Miss) D. M. Crowfoot, William Sage Rapson, and Robert Robinson.

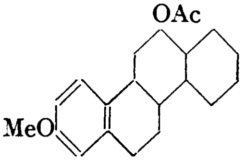
Certain examples of the new synthetic process described in Part II (J., 1935, 1285) are of especial interest in view of the close constitutional relation of the products with the female sex-hormones and also because favourable yields are obtainable from accessible materials. Cook and Hewett (this vol., p. 64), whilst admitting that these substances "probably contain condensed hydroaromatic systems," remark that the structures of the products have not been proved.

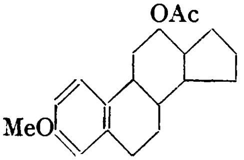
Nevertheless, the only alternatives to our suggested formulæ are inherently improbable. For example, in the condensation of 6-methoxy-α-tetralone with acetyl*cyclo*hexene the possibilities are (I), (II), and (III), of which (I) was selected. The expressions (II) and (III) were excluded because the general properties of the product were not in good agreement with such formulations and also for the specific reason that catalytic reduction afforded a tetrahydro-derivative of alcoholic rather than ketonic function. The prepar-


(I.)


(II.)


(III.)

(IV.)



(V.)

ation of the acetyl derivatives (IV) and (V) was actually carried out before Part II wa published, although the absence of ketonic behaviour of the tetrahydro-derivatives wa already patent. The X-ray crystal analysis is in harmony with the proposed structure which are further confirmed by the results recorded in the two succeeding parts of thi series.

EXPERIMENTAL.

2-*Acetoxy*-10-*methoxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-*dodecahydrochrysene* (IV).—The hydrogenation product of ketomethoxydecahydrochrysene (Part II, *loc. cit.*) does not reac with Brady's reagent, although all ketones of this series do so with facility. On heating wit acetic anhydride for 3 hours on the steam-bath, the *acetate* was obtained; this crystallise from methyl alcohol in glistening needles, m. p. 155—156° (Found : C, 76·9; H, 8·5. $C_{21}H_{28}O$ requires C, 76·8; H, 8·5%). The corresponding methoxy*cyclo*pentanophenanthrene *derivativ* (V), obtained in a similar fashion, crystallised from methyl alcohol in slender needles, m. p 102—103° (Found : C, 76·4; H, 8·3. $C_{20}H_{26}O_3$ requires C, 76·4; H, 8·3%).

Crystallographic Data.—3-*Hydroxy*-7-*methoxy*-3 : 4 : 9 : 10 : 11 : 12-*hexahydro*-1 : 2-cyclo-*pentanophenanthrene* (alcohol related to the acetate V). This compound formed needles much elongated along the b axis and flattened on (001). The extinction was straight with α along b and γ inclined at about 21° to the normal to the c plane.

The unit cell dimensions were : $a = 7{\cdot}5$, $b = 5{\cdot}3$, $c = 35{\cdot}1$ A., $\beta = 98°$; $h0l$ halved for l odd; $0k0$ halved for k odd; space group, $P2_1/c$; $n = 4$ if $\rho = 1{\cdot}29$.

The optical data and intensities suggest that the molecules are arranged as a four-layer structure in the c plane, the long axis being mainly along γ and the short axis somewhat inclined to the b plane.

The structure is of particular interest since it requires the presence of two identical pairs of molecules related by a glide plane of symmetry, that is, of pairs of enantiomorphous molecules.

2-*Hydroxy*-10-*methoxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 13 : 14 : 15 : 16-*dodecahydrochrysene* (alcohol related to the acetate IV). From methyl alcohol this substance afforded long needles which rapidly became opaque on exposure to air. They therefore probably contained solvent of crystallisation and were not further investigated.

From light petroleum three forms separated :

A. Large, very fine tetragonal crystals showing well-developed prism and pyramid faces; optically they were positive.

The X-ray measurements gave : $a = 15{\cdot}6$, $c = 12{\cdot}8$ A.; hkl absent for $h + k + l$ odd; $n = 8$ for $\rho = 1{\cdot}21$. There are no planes of symmetry and the space group is probably $I4$ or $I\bar{4}$. This is a very unusual type of crystal structure. The molecules are probably fitted into the cell with their long axes along c and short axes parallel or nearly so to a, since the 200 and 400 reflections are very powerful.

B. Very long needles. These very fine needles, much elongated along a, showed a crossed extinction as usually viewed, but straight at right angles to this direction. It was difficult to determine exactly the optic orientation, but α is probably at about 30° to the a axis.

The dimensions of the unit cell are : $a = 5{\cdot}2$, $b = 24{\cdot}7$, $c = 14{\cdot}7$ A., $\beta = 128°$; $a \sin \beta = 4{\cdot}1$; $c \sin \beta = 11{\cdot}5$ A.; $0k0$ absent for k odd; space group, $P2_1$; $n = 4$ for $\rho = 1{\cdot}27$. There are two molecules in the asymmetric unit and the arrangement is probably such that thickness is mainly in the a plane and length along b. There seems no simple connexion between this and A.

C. This form consisted of small needles elongated along b and flattened on (100). Optically it appeared orthorhombic or pseudo-orthorhombic with α along b, β in a and γ in c. The crystals were very small and gave few X-ray reflections. It is almost certain that the true dimensions are some multiple of the following : $a = 14{\cdot}6$, $b = 4{\cdot}16$, $c = 14{\cdot}0$ A.

That the three forms are truly polymorphic modifications of one and the same substance is indicated by the following observations. On crystallisation from methyl alcohol, only one type of crystal form was observed—the needle-shaped variety probably containing solvent. On melting, all three forms could be induced to pass into the same modification A. This was most difficult to obtain from C and was only observed after seeding. If A is kept melted for some time and then cooled suddenly, all three forms are occasionally produced. They are easily distinguished in polarised light, since in B the extinction appears crossed with reference to the needle axis and in A this axis is the slow extinction, in C the fast.

2-*Keto*-10-*methoxy*-2 : 3 : 4 : 5 : 6 : 7 : 8 : 14 : 15 : 16-*decahydrochrysene* (I). This compound occurs as fine needles, very much elongated along a. All the crystals examined proved to be very close twins which although monoclinic simulated orthorhombic symmetry closely.

The dimensions of the monoclinic unit were: $a = 8{\cdot}3$ A. α, $b = 15{\cdot}65$ A. γ, $c = 12{\cdot}3$ A. β, $\beta = 109°$; $0k0$ absent for k odd; $h0l$ absent for $h + l$ odd (?). It is a little difficult to make sure of the halvings owing to the twin character of the crystals. Space group, $P2_1/n$; $n = 4$ for $\rho = 1{\cdot}22$. The pseudo-orthorhombic cell formed by twinning has $a = 8{\cdot}3$, $b = 15{\cdot}65$, $c = 23{\cdot}8$ A.; hkl halved for $h + l$ halved.

Optically, in spite of the monoclinic symmetry, the extinction appeared straight along the needle. The birefringence was high, positive, and the optic axial angle small.

3-*Keto*-7-*methoxy*-3 : 9 : 10 : 11-*tetrahydro*-1 : 2-cyclo*pentanophenanthrene*. This is very similar to its ring homologue (I). The crystals are needles elongated along the a axis and showing a straight extinction. As in the case of (I), they are invariably twins simulating orthorhombic symmetry. The cell dimensions are probably as given below, but the crystals, being very small, gave very weak reflections and no planes observed indicated an a axis longer than 4·05 A.: $a = 8{\cdot}1$, $b = 14{\cdot}65$, $c = 12{\cdot}15$ A., $\beta = 112°$; $n = 4$ for $\rho = 1{\cdot}255$. For the orthorhombic apparent cell: $a = 8{\cdot}1$ (/2), $b = 14{\cdot}65$, $c = 23{\cdot}70$ (/2), A. The optical character is exactly similar to that of (I) described above.

THE DYSON PERRINS LABORATORY AND THE DEPARTMENT OF MINERALOGY,
OXFORD UNIVERSITY.

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