

equilibrium specific rotation of *d*-glucose in absolute ethanol are in error. The data given in the "Tables" are taken from the work of Hudson and Yanovsky⁵ and apply to absolute methanol, not absolute ethanol.

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Note on the Arrangement of Phases in Palladium-Hydrogen

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The existent studies of palladium by methods of X-ray diffraction, now more than a dozen in number,² show the system to include two phases, both of face centered cubic type, but of widely differing lattice constants, and having compositions which vary over considerable ranges. Since these investigations have been carried out under conditions not suited to make clear the spatial arrangement of the phases, it seemed desirable to show that, as is to be expected in a diffusion system, the two phases of this typical hydrogen alloy are completely segregated, and that changes in gross composition are accompanied by migration of the phase boundary.

The palladium used was about 99.85% pure and had the form of a ribbon of 5×0.05 mm. cross section. This ribbon was suspended vertically in a tube 2 cm. in diameter, consisting of thin celluloid cemented to glass end-pieces, which was borne by an adjustable support provided with a vertical scale. A back reflection camera was employed, with a slit system such that the irradiated area on the specimen extended one millimeter vertically by four millimeters across the strip horizontally. The target was of iron, and the distance between specimen and film was 6 cm. The containing tube was filled to 3.2 cm. above the bottom of the ribbon with 2 *N* sulfuric acid, and during the series of observations the palladium was continuously charged by passing into the immersed portion a current of 5 milliamperes from an adjacent anode of platinum foil. The palladium at the level of the electrolyte had therefore a fixed hydrogen concentration corresponding to a cathodic current density of approximately 0.16 amp./sq. dm.

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(2) Most recent studies E. A. Owen and J. Idwal Jones, *Proc. Phys. Soc. London*, **49**, 587, 603 (1937); A. Michel, *Bull. assoc. tech. fonderie*, **12**, 302 (1938).

Preliminary exposures, made after some hours of electrolysis, gave the diffraction spectrum of the β phase only, from a region in the palladium one millimeter above the electrolyte level; while at a point several millimeters higher, the spectrum of the α phase was alone observed. It was also found that whereas exposures of three-quarters of an hour were required to yield a visible β phase pattern on an unrotated film, diffraction from the α phase was sufficiently intense to give a clear result in ten minutes. For following the progress of the diffusion, exposures of ten or fifteen minutes were therefore made, and the absence of any pattern was taken as showing the presence of the β phase in the region observed. The results are displayed in Table I, where time is taken from the beginning of measurements, after the full saturation of the metal below the electrolyte, and distance is measured upward from the level of the liquid.

TABLE I

Film	Time, hr.	Distance, mm.	Phase	Rate of boundary migration
12	4.5	4	α	\approx 1 mm. in 5 hr., or 0.20 mm./hr.
13	5.0	1	β	
14	5.7	3	α	
15	22.5	3	β	\approx 4 mm. in 23.3 hr., or 0.17 mm./hr.
16	23.3	5	α	
18	24.3	4	α	
20	46.5	4	β	\approx 6 mm. in 47.6 hr., or 0.126 mm./hr.
21	47.6	6	α	
22	50.7	7	α	

As may be seen from this table, the boundary steadily advanced from the line at which the hydrogen concentration was kept constant, the rate declining from a value exceeding 0.20 mm. per hour to a value less than 0.126.

The method employed could doubtless be made to serve for exact observation of the rate of diffusion, unaffected by factors introduced by the entry and exit of hydrogen at the metal surfaces. Since this, however, would involve a determination of the relation between the cathodic current density and the hydrogen concentration attained in the cathode, and since the diffusion constant obtained would be valid for the metal only in the precise physical condition in which it was examined, we have here contented ourselves with demonstration of the qualitative relationships.

The results show clearly the division of the alloy into two distinct phases, one of which (α) occupies all of the region in which the concentration of hydrogen is below a certain saturation

limit; while the other phase (β) is present alone wherever this limit is exceeded. They also make plain the migration of the phase boundary with continued diffusion. Finally they show that the higher order diffraction lines from the β phase are much less intense than those of the α phase, a

fact probably due to the severe cold working which occurs as β is formed from α by a sudden expansion of over 3% (linear) at the advancing phase boundary.

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COMMUNICATIONS TO THE EDITOR

STRUCTURE OF CANNABIDIOL. VIII. POSITION OF THE DOUBLE BONDS IN CANNABIDIOL. MARIHUANA ACTIVITY OF TETRAHYDRO-CANNABINOLS

Sir:

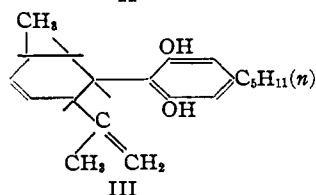
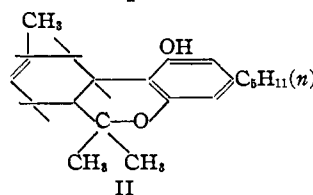
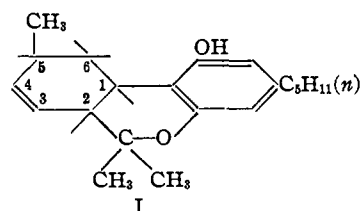
Certain mild reagents (previous papers V, VI) convert cannabidiol into a tetrahydrocannabinol $[\alpha]^{32D} -165 \pm 7^\circ$; more vigorous reagents to one with $[\alpha]^{32D} -240 \pm 10^\circ$. It is obvious from the rotations that these forms are not absolutely pure and each is probably contaminated with the other.

The lower-rotating tetrahydrocannabinol can be converted to the higher-rotating by the same reagents and under the same conditions which convert cannabidiol to the higher-rotating form; thus the lower-rotating form is presumably the initial reaction product in the isomerization of cannabidiol and the higher-rotating form a secondary product. Therefore, the lower-rotating form probably has the double bond in the same position as the corresponding double bond in cannabidiol.

Cannabidiol has been shown to have no double bond conjugated to the benzene ring; that its two double bonds are not conjugated to each other is indicated by the very close values of the absorption spectrum of cannabidiol (maximum $\log \epsilon$, 3.18), and that of tetrahydrocannabidiol (3.05) and confirmed experimentally by failure of repeated attempts to condense cannabidiol dimethyl ether with maleic anhydride. The double bond in each of the tetrahydrocannabinols has been shown not to be conjugated to the aromatic nucleus by comparison of their physical constants with that of a synthetic tetrahydrocannabinol of unequivocal constitution with the double bond conjugated (see paper VII). Positions 1,2 or 1,6

or 2,3 for the ring double bond in cannabidiol or in the tetrahydrocannabinols are thus excluded.

The migration of the double bond in the tetrahydrocannabinol, if 2,3 or 5,6, should proceed to the most favored position, in conjugation with the benzene ring. As this does not occur, positions 3,4 and 4,5 remain and are considered the most probable. The 3,4 is assigned to the lower-rotating tetrahydrocannabinol (I) and the 4,5 to the higher-rotating (II), for migration from the 3,4 to the 4,5 position (which has the methyl substitution) is more likely than *vice versa*. Through its relationship to the lower-rotating tetrahydrocannabinol, cannabidiol may be postulated as having structure III.



The tetrahydrocannabinols have a very potent marihuana activity which is markedly greater