

proton and electron are detached and emitted as a neutron leaving carbon 12, as postulated by Chadwick [*Nature*, **129**, 312 (1932)].

The essential point may be stated in this way. In the proposed structure alpha particles and neutrons do not exist as such in any nucleus, merely protons and electrons coupled in a certain definite pattern. When these couplings are broken, alpha particles and electrons in pairs are normally formed as in the radioactive series. However, it should also be possible to break the bonds in such a way as to give neutrons, mass one or two, hydrogen, mass one or two, helium mass 5, etc., and it is to be expected that such particles would be formed more readily from nuclei containing unsymmetrical or unsaturated groups.

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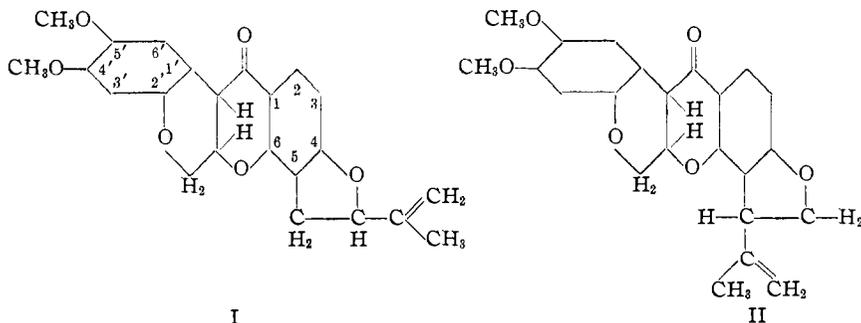
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ROTENONE. XXI. THE STRUCTURE OF ISOROTENONE,
 β -DIHYDROROTENONE AND DEHYDROROTENOL

Sir:

In a recent publication [S. Takei, S. Miyajima and M. Ōno, *Bul. Inst. Phys. and Chem. Research* (Tokyo), **11**, 1-4, Feb. 1932] Takei and his associates proposed a formula for rotenone which differs from the one (I) proposed by us [F. B. LaForge and H. L. Haller, *THIS JOURNAL*, **54**, 810 (1932)] only in the point of attachment of the isopropenyl side chain on the substituted dihydrocoumarone ring as indicated in formula II.

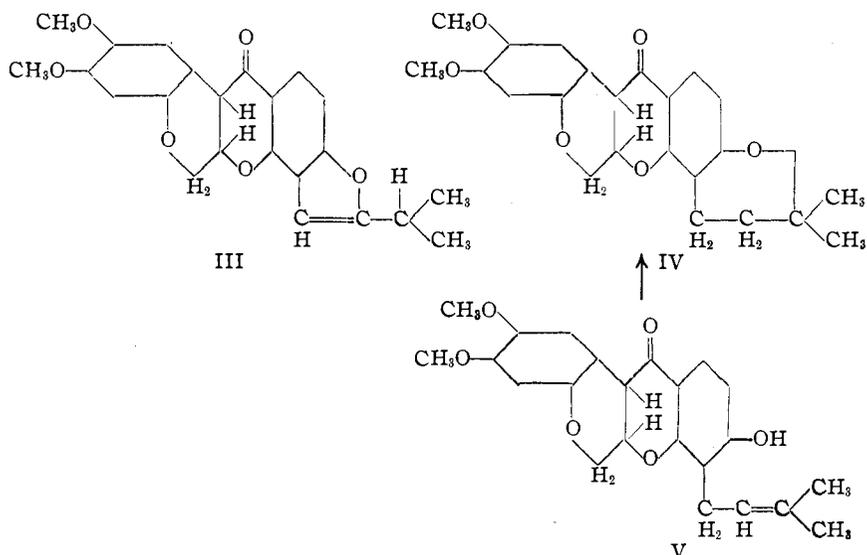


The formula of Takei takes no account of the loss of optical activity by cleavage of the oxygen bridge with the resultant formation of the phenolic hydroxyl in position 4 by hydrogenation of tubaic acid and the analogous formation of tetrahydro derivatives from other rotenone derivatives. Moreover, the mechanism suggested by us is strongly supported by analogy with that of certain codeine derivatives, which is referred to in a previous article [H. L. Haller and F. B. LaForge, *THIS JOURNAL*, **54**, 1988 (1932)].

Both these results are to be expected from the groupings present in formula I but would not be possible according to Takei's formula II.

As the complete formula for rotenone is now known, it is possible to propose a formula for isorotenone [S. Takei, *Biochem. Z.*, **157**, 1 (1925); *Ber.*, **61**, 1003 (1928)] and for β -dihydrorotenone. [H. L. Haller, *THIS JOURNAL*, **53**, 733 (1931)]. However, a modification of the structure proposed for dehydrorotenol [H. L. Haller and F. B. LaForge, *THIS JOURNAL*, **53**, 2271 (1931); F. B. LaForge, H. L. Haller, and L. E. Smith, *THIS JOURNAL*, **53**, 4403 (1931)] is necessary.

It has been shown that rotenone and isorotenone differ from each other in the position of a double bond. Therefore, structure III, which accounts for all the facts, is proposed for isorotenone.



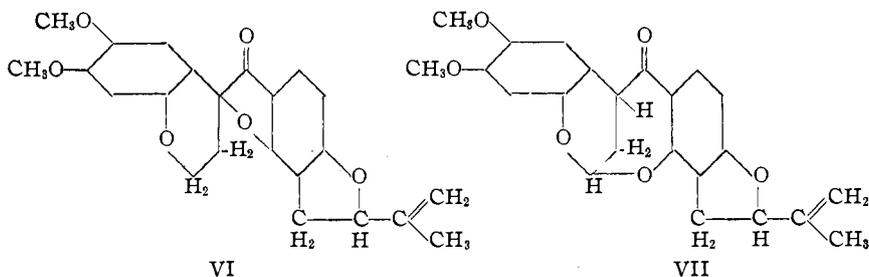
β -Dihydrorotenone (IV), an isomer of dihydrorotenone, which gives many of the typical reactions of dihydrorotenone, is obtained when rotenonic acid (V) is dissolved in a solution of acetic and sulfuric acids. The formation of β -dihydrorotenone is in a measure analogous to the formation of a saturated lactone by the isomerization of an unsaturated acid.

Dehydrorotenol, which is obtained on mild oxidation of rotenol, is colorless, unlike all other dehydro derivatives of the rotenone series, which are yellow. It also differs from these in that it can be reconverted into rotenol by reduction.

Dehydrorotenol, like rotenol, can be hydrogenated to a tetrahydro derivative which is alkali soluble but which differs from the tetrahydrorotenol (dihydrorotenolic acid) in that it is not cleaved by alkaline hydrogen peroxide. Rotenol possesses a free hydroxyl group in the tubaic acid half of the

molecule, and this free hydroxyl group is essential for the cleavage of the carbonyl group with alkaline hydrogen peroxide. It follows therefore that this group is not present in dehydrorotenol. Rotenol gives a color test with ferric chloride, whereas dehydrorotenol does not. Thus it follows that the hydrogen atom of the free hydroxyl group is involved in the formation of dehydrorotenol. If the original ether linkage in rotenone was reformed in the formation of dehydrorotenol from rotenol, dehydrodihydro-rotenolic acid and *dl*-dihydrorotenonic acid [H. L. Haller and F. B. LaForge, THIS JOURNAL, 53, 3426 (1931)] should be identical as the asymmetric center I [*ibid.*, p. 3427] is racemized in the formation of rotenol. Besides, dehydrorotenol does not react with iodine and alcoholic potassium acetate to lose two hydrogen atoms and to form dehydrodihydrorotenone. It is possible, therefore, that the structure for dehydrorotenol is either VI or VII.

The product obtained from dehydrodihydrorotenolic acid and acetic anhydride, which was thought to be a mixed anhydride [H. L. Haller and F. B. LaForge, THIS JOURNAL, 53, 2271 (1931)], is in fact a true acetyl derivative, the hydroxyl group in the 4 position having been acetylated.



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THE RELATION BETWEEN THE DISSOLUTION OF METALS IN ACIDS AND THE ELECTROLYTIC EVOLUTION OF HYDROGEN

Sir:

The finding of Brönsted and Kane [THIS JOURNAL, 53, 3624 (1931)] that the velocity of the reaction of sodium amalgam with aqueous solutions is proportional to a fractional power of the concentration of sodium in the amalgam suggests strongly that the rate of hydrogen evolution on a sodium amalgam surface is essentially the same as on a mercury surface polarized electrically to a potential equal to that established by the sodium-sodium ion equilibrium. From the precise and definitive work of Bowden [*Trans.*