LETTER

The Relation Between the Structure of γ-Lactones and the Vaule of their Molecular Rotations — Presumption of Eight Unknown $[M]_D^{20}$

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C. S. Hudson reported of the quantitative relation between the structure of γ-lactones and the value of their molecular rotations and calculated $[M]_D^{20}$ of six lactones, now unknown. However, since his view had no ground of physical theory, he could not explain the fact that the optical rotatory power of C^5 atom in lactones of Xylonic-Lyxonic type is opposite in sign to that in lactones of Ribonic-Arabonic type.[1] The author tried to apply physical theories of the optical rotation to this idea, and found some empirical rules concerning the quantitative relation from the standpoint of the arrangement of atoms, and by using these rules, he presumed eight unknown $[M]_D^{20}$.

At first, all of γ-lactones are divided into Ribonic-, Arabonic-, Lyxonic-, and Xylonic-types according to the types of their own rings. Next, $[M]_D^{20}$-change accompanying the change of the side-chain is classified into two parts, one of which corresponds to the change of the end-group or the length of the side-chain in the case when the number of asymmetric atom is constant (G-change), and the other of which corresponds to the change of the number of asymmetric atom in the side-chain in the case when the end-group and the length of the side-chain is constant (O-change). The physical meaning of G-change is the $[M]_D^{20}$-change accompanying the change of the degree of induced dissymmetry of the CO-group[2] in the γ-lactone-ring, under the influence of the chain-length and the chain-end-group. The physical meaning of O-change is the $[M]_D^{20}$-change accompanying the appearance of a new asymmetric atom which has its own optical rotatory power. Then the optical rotatory power of the ring itself is not constant in all types, even in R-type, contrary to the Hudson's view. Now the theory of the optical rotatory power of J. G. Kirkwood, based upon the quantum-mechanics,[3] was used to explain O-change at C^5, by using examples of L-talonic-, D-allonic-, L-galactonic-, D-altronic-, L-gulonic-, D-mannonic-, L-idonic-, and D-gluconic-γ-lactones, with success. The outline of his theory is as follows: he calculated the $[M]_D^{20}$ of D-secondary butyl alcohol and concluded that free rotation of the (CH_3) (H) (OH)-C*- group around the axis of C*-C_2H_5 is possible, and the end-group (CH_3) of the ethyl group can be placed under (CH_3), (H) or (OH), each bound to C*. The $[M]_D^{20}$ of the molecule changes according to the place of the end-group (CH_3) described above. The case when the (C_2H_5) group of D-secondary butyl alcohol is replaced by the γ-lactone-ring is now under discussion.

Possibility of free rotation of the side-chain around the axis of C^5-C^4, makes O-changes of R- and A-types equal; but, in L- and X-type, it is hindered by O-atom, bound to C^3, and H, bound to C^5, is forced to stand upon C^3. This configuration causes revision of the sign of O-change. Thus, the first rule was deduced: "Each of C atoms in a definite side-chain, whether this chain attaches to R- or A-type-ring, causes O-change of its own constant value." Using this rule, and data of L-epifuconic-, D-allomethylonic-, and L-fuconic-γ lactones, the $[M]_D^{20}$ of D-altromethylonic-γ-lactone was presumed. Using the first rule, other six unknown $[M]_D^{20}$ values —these six have already been calculated by Hudson—were calculated. Two more rules were induced from data. The second rule: "Replacement of (CH_2OH) by (CH_3) at the end of the side-chain causes no large change in O-change". The third rule: "Entfernungssatz der Drehung of L. Tschugaeff[4] is seen in O- and G-changes, and the magnitude of G-change, caused by replacement of end-group (CH_2OH) by (CH_3) at α-position of the side-chain is 1.9 times of that at β-position". Using

(1) C. S. Hudson, *J. Am. Chem. Soc.*, **61**, 1525 (1939).
(2) T. L. Harris, E. L. Hirst and C. E. Wood, *J. Chem. Phys.*, **2**, 1825 (1934).
(3) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937); **7**, 139 (1939).
(4) L. Tschugaeff, *Ber.*, **31**, 360 (1898).

this rule, the $[M]_D^{20}$ of D-ribonic-γ-lactone was calculated. The presumed values of $[M]_D^{20}$ of γ-lactones are as follows; a-D-alloheptonic-, -20.1; L-talloheptonic-, 1.2; D-gala-L-talo-octonic-, 84.7; D-ribomethylonic-, -1.9; D-allo-D-altroheptonic-, 59.9; D-gulo-L-gala-heptonic-, 133.0; L-talo-D-altroheptonic-, 81.2; D-altromethylonic-, 28.4; six of these are different from those, presumed by Hudson by about two degrees in the magnitude of $[\alpha]_D^{20}$.

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