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CIRCULAR DICHROISM OF GIBBERELLINS AND THE APPLICATION OF THE LACTONE CHROMOPHORE TO THEIR STRUCTURAL ELUCIDATION

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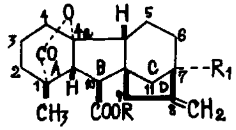
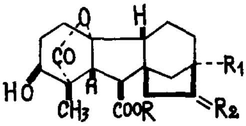
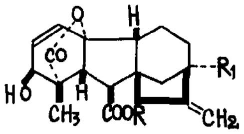
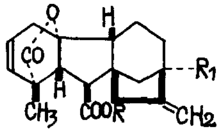
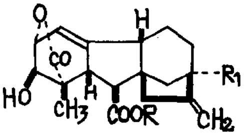
The combined physicochemical methods such as ultraviolet, infrared, nuclear magnetic resonance (1) and mass spectroscopy (2) made possible to determine the structures of small quantities of new gibberellins. Optical rotatory dispersion (ORD) and circular dichroism (CD) have been used for the elucidation of stereochemistry of gibberellins after introduction of a ketone at C-7 or C-8 (3).

Here we report CD of some C_{19} gibberellins and their methyl esters as well as some other related compounds at the wave length of 200-300 mμ and its application to the stereochemistry and structural elucidation. CD were measured with a Japan Spectroscopic Model ORD/UV-5 recording polarimeter with CD attachment at room temperature (16-30°C). Sample solutions were prepared by dissolving about 1 mg of the samples in 2 ml of ethanol. Quarz cells with an optical path of 1.0 cm or 0.1 cm were used for measurement.

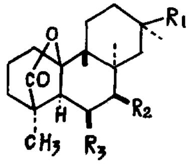
Gibberellins and their methyl esters have two carbonyl chromophores, a γ-lactone at C-1 and a carboxyl or carbomethoxyl at C-10 in gibbane skeleton, and their ORD showed overlapped Cotton effects due to these two chromophores. Because of the possible free rotation of the C-10 carboxyl group and its high intensity, theoretical interpretation of the ORD was difficult. However in CD a lactone peak at about 225 mμ was distinguished from the back ground of the carboxyl or the carbomethoxyl peak.

Table

	R	R_1	R_2	Wave length (mμ)	$[\theta]\times10^{-3}$	Temp.
(I) 						
A_{20}-Me	CH_3	OH		225	- 4.6	20°C
A_9-Me	CH_3	H		222	- 5.3	16°C
(II) 						
A_1	H	OH	CH_2	222	- 2.3	18°C
A_1-Me	CH_3	OH	CH_2	226	- 2.3	18°C
A_4	H	H	CH_2	222	- 2.0	18°C
A_4-Me	CH_3	H	CH_2	222	- 1.5	18°C
A_2	H	H	OH, CH_3	222	- 3.2	17°C
A_2-Me	CH_3	H	OH, CH_3	224	- 1.5	16°C
dihydro A_1-Me	CH_3	OH	H, CH_3	223	- 1.7	16°C
(III) 						
A_3	H	OH		232	- 2.8	18°C
A_3-Me	CH_3	OH		230	- 2.5	11°C
A_7	H	H		228	- 1.9	20°C
A_7-Me	CH_3	H		230	- 3.7	18°C
(IV) 						
A_5	H	OH		224	-83.2	22°C
A_5-Me	CH_3	OH		222	-66.4	18°C
deoxy A_5	H	H		222	-84.7	28°C
deoxy A_5-Me	CH_3	H		222	-85.6	30°C
(V) 						
iso A_3-Me	CH_3	OH		226	- 8.0	18°C
iso A_7	H	H		224	- 8.9	17°C
iso A_7-Me	CH_3	H		226	- 6.9	17°C

The molecular elipticities ([θ]) at the maximum are shown in Table. Relationship between [θ] and structure can be summarized as follows.

(a) All the gibberellins whose lactone is α to A ring gave a negative sign. It, together with the positive sign of the lactone in rosenonolactones (VI) which is β to A ring (4,5), suggests the application of the sign to determine the stereochemistry of C-1∿C-4a lactone of new gibberellins.



(VI)

(b) The intensity of the lactone peak was sensitive to the structural modifications of A ring which located near the lactone carbonyl but was less affected by the C-10 esterification and structural changes in C and D rings which located in the distance. It suggests an application of the [θ] at the extrema to the structural study of A ring such as the presence of the C-2 hydroxyl and the position of double bond. Thus esters of (I) which have neither hydroxyl group nor double bond in A ring gave CD extrema about two times more intense than those of (II) which have β-hydroxy at C-2. The methyl esters of (III) which have C-3∿C-4 double bond and β-hydroxy at C-2 gave slightly higher [θ] than those of (II) and their maxima were found at 230 mμ which showed a red shift of about 5 mμ from those of (I) and (II). The compounds (IV) which have C-2∿C-3 double bond or β,γ-unsaturated lactone gave a extremely strong peak, whose intensity is about fifteen times higher than those of (I). The free gibberellins gave similar tendencies to their methyl esters.

Theoretically it should be noted that the gibberellins of (I), (II) and (III), as well as rosenonolactone, are compatible with the Lactone Sector Rule by Klyne (6), if the near atoms in or directly attach at A ring can contribute the sign and those atoms in B, C and D rings are negligible. It is important that the β,γ-unsaturated lactone (IV) gave a very strong peak but showed no wavelength shift from that of saturated lactones. In the case of β,γ-unsaturated ketone the similar phenomenon has been known. Moscowitz (7) explained it by formation of a kind of inherently dissymmetric chromophore by interaction of n-electrons of carbonyl with the π-electrons of β-γ double bond and cited the application of their sign and strength to determine the relative geometry of the carbonyl and the double bond. In analogy with the ketone this high intensity suggests the similar interaction between the lactone carbonyl and the double bond, and hence the similar application of CD to determine their relative geometry. The high intensity of isogibberellins (V) and their discrepancy with the Lactone Sector Rule may be explained by the formation of inherently dissymetric chromophore which might cancell the skeleton contribution.

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