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The magnetic circular dichroism (MCD) spectra of some 3-arylfervenulins and 3-aryltoxoflavins were measured. From the dependence of the Faraday B values of 3-arylfervenulins and 3-aryltoxoflavins on the Hammett σ_{para} values, it is concluded that the substituent effects on the Faraday B values of 3-aryltoxoflavins are reverse to the substituent effects on the Faraday B values of 3-arylfervenulins and the reverse property of 3-aryltoxoflavins concerning the substituent effects rises from the contribution of the 1,5-dipolar structure of 3-aryltoxoflavins.

J. Heterocyclic Chem., 15, 615 (1978).

The antibiotics ferverulin (1-4) and toxoflavin (5,6), derivatives of the pyrimido[5,4-*e*]-*as*-triazine (7-azapteridine), have aroused considerable recent interest in the chemistry and biology of this ring system (7), because of their strong physiological and antimicrobial activities. The electronic structures of these compounds are also of interest in connection with their chemical reactivity viewpoints (8,9).

The magnetic circular dichroism (MCD) spectra have some advantage over ordinary spectrophotometric techniques in that the occurrence of a negative band and the sharp sensitivity to changes of electronic structures are observed. Because of this sensitivity, the MCD spectra give valuable information with respect to structural differences between similar compounds (10).

In order to clarify the differences of the electronic structures of ferverulin and toxoflavin skeletons, we measured the MCD spectra of 3-arylfervenulins (Ia, Ib and Ic) and 3-aryltoxoflavins (IIa, IIb and IIc).

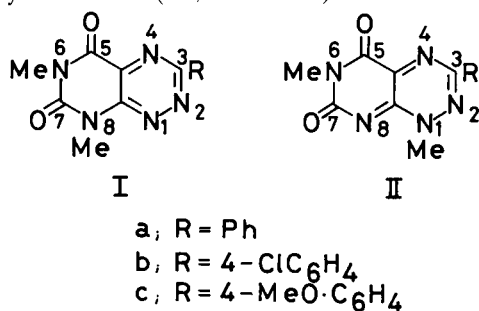


Figure I. 3-Arylfervenulins and 3-Aryltoxoflavins.

As the MCD and uv spectra of Ia, Ib and Ic resemble each other, the MCD and uv spectra of Ia as a representative were given in Figure II. The MCD and uv spectra of IIb and IIc were almost the same as the MCD and uv spectra of IIa. Figure III shows the MCD and uv spectra of IIa. The negative and positive bands of the MCD spectra

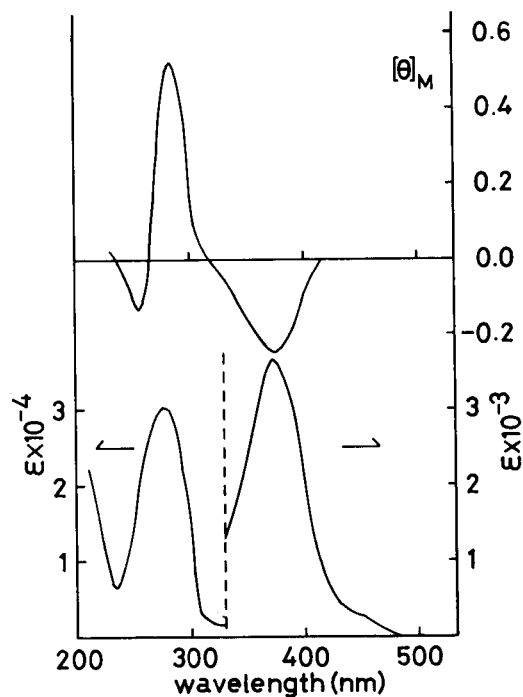


Figure II. The MCD (top) and Uv (bottom) Spectra of 3-Arylfervenulin in Ethanol.

correspond to the first (at about 400 nm) and second (at about 280 nm) bands of the uv spectra, respectively.

The molecular symmetry of Ia, Ib, Ic, IIa, IIb and IIc is so low that only the Faraday parameter B is extracted from the MCD spectra of these compounds. The Faraday parameter B is evaluated using the formula:

$$B = -(33.53)^{-1} \int_{\text{band}} ([\theta]_M / \nu) d\nu$$

where ν is frequency in cm^{-1} and $[\theta]_M$ is molar ellipticity per unit field in units of $\text{deg l m}^{-1} \text{ mole}^{-1} \text{ gauss}^{-1}$ (11). The MCD spectra are analyzed assuming Gauss-type absorption bands with the method described by Badoz, *et al.*, (12). The extracted Faraday parameter B is summarized in Table I.

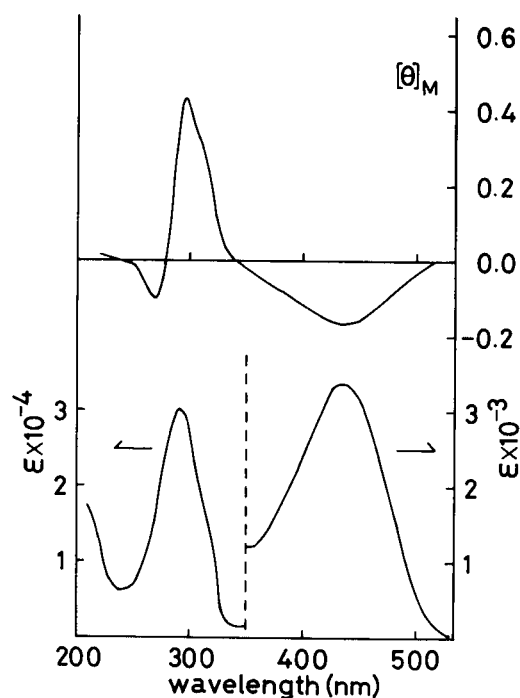


Figure III. The MCD (top) and Uv (bottom) Spectra of 3-Aryltoxoflavin in Ethanol.

Table I

Absorption Maximum (ν_{\max}) and Faraday Parameter (B)

Compound	ν_{\max} (a)	B (b)
Ia	26.74	1.07
	36.50	-1.43
Ib	26.60	1.18
	35.09	-1.32
Ic	25.32	0.94
	33.11	-1.55
IIa	23.10	1.07
	34.48	-1.30
IIb	22.94	1.04
	33.78	-1.32
IIc	21.93	1.13
	32.26	-1.25

(a) In 10^3 cm^{-1} . (b) In $10^{-3} \text{ debye}^2 \text{ Bohr magneton/cm}^{-1}$.

Foss and McCarville (13) have found that there is a correlation between the magnitude and sign of the MCD of a series of substituted benzenes and the substituent's Hammett σ_{para} value (14) for both the mono- and di-substituted. The Faraday B values of the first bands of Ia, Ib, Ic, IIa, IIb and IIc against the Hammett σ_{para} values are shown in Figure IV. Figure IV shows the facts that as the Hammett σ_{para} values increase the Faraday B values of 3-arylfervenulins increase and the Faraday B values of 3-aryltoxoflavins decrease. The plot of the absolute values

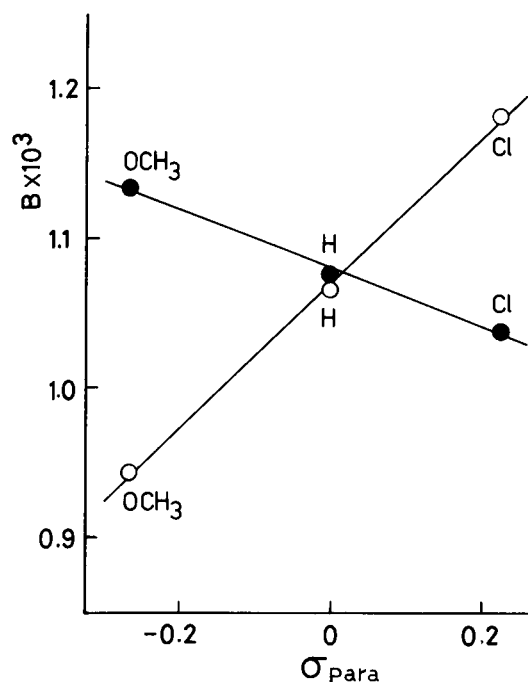


Figure IV. The Plot of the Faraday B Values of the First Bands of 3-Arylfervenulins (white circles) and 3-Aryltoxoflavins (black circles) against the Hammett σ_{para} Values.

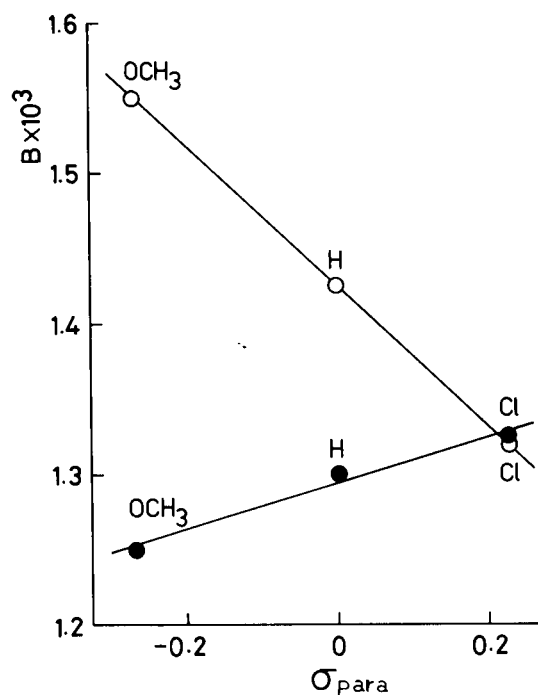


Figure V. The Plot of the Faraday B Values of the Second Bands of 3-Arylfervenulins (white circles) and 3-Aryltoxoflavins (black circles) against the Hammett σ_{para} Values.

of the Faraday B of the second bands of Ia, Ib, Ic, IIa, IIb and IIc against the Hammett σ_{para} values is indicated in Figure V. From Figure V, it is found that when the Hammett σ_{para} values increase the Faraday B values of

3-arylfervenulins decrease and the Faraday B values of 3-aryltioxflavins increase.

The quantum mechanical equation for the Faraday B term is expressed by the magnetic transition moments, electric transition moments and transition energies among various electronic states (15). The changes in the Faraday B values induced by substituents may arise from changes in the electric transition moments, changes in the magnetic transition moments and changes in the energy levels. As the equation is very complicated, it is very difficult to obtain directly the informations for electronic structures of these complicated molecules by using the equation. If it could be assumed that the changes in the electric transition moments might be almost the same and the changes in the energy levels might parallel the changes in the magnetic transition moments in the series of 3-arylfervenulins and 3-aryltioxflavins, the changes of the Faraday B values might be proportional to the magnitude of changes in the magnetic moments. According to the electromagnetic theory (16), the magnitude of the magnetic moment is proportional to an amount of electron flowing in the framework of molecule.

The first band of Ia may be originated from a transition related with the electron migration from nitrogen to carbonyl oxygen as shown in (A) of Figure VI. It is considered that the electron migration is enhanced by the

The first band of IIa may arise from the electron migration illustrated in (B') of Figure VI. In this case it is considered that when the contribution of the 1,5-dipolar structure becomes greater, the electron migration indicated in (B') is enhanced. Since the presence of the electron-withdrawing chlorine atom of IIb weakens the contribution of the dipolar structure and consequently the electron migration is impeded, the Faraday B value of IIb becomes smaller than the Faraday B value of IIa. On the other hand, as the presence of the electron-donating methoxy group of IIc raises the contribution of the dipolar structure and enhances the electron migration, it is expected that the Faraday B value of IIc becomes larger than the Faraday B value of IIa. As the second band of IIa probably comes from a transition involving the electron migration indicated in (C') of Figure VI, it is considered that the substituent effect on this band is reverse to the substituent effect on the first band.

It can be concluded that the substituent effect on the Faraday B values of 3-aryltioxflavins are the very reverse to the substituent effect on the Faraday B values of 3-arylfervenulins.

EXPERIMENTAL

Chemical.

Compounds Ia, Ib, Ic, IIa, IIb and IIc were prepared according to the reported procedures (4,6). These compounds were recrystallized twice from ethanol. Ethanol was carefully purified according to the descriptions in reference (17).

Measurements.

The uv spectra were taken on a Shimadzu UV-200 recording spectrophotometer. The MCD spectra were measured on a JASCO J-40 AS recording spectropolarimeter equipped with a 3.5 k gauss permanent-magnet. All measurements were made on deaerated samples at room temperature.

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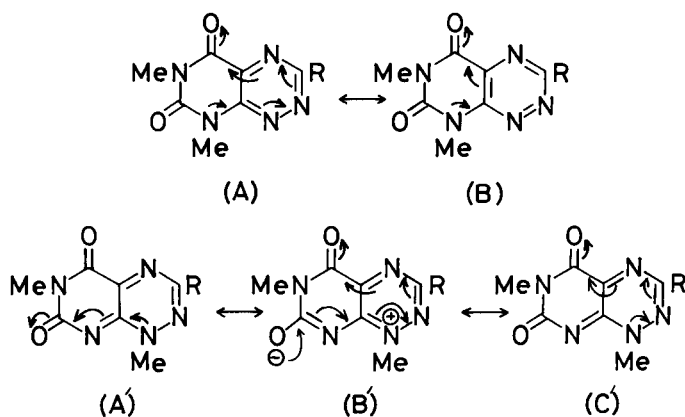


Figure VI. The Electron Migration of 3-Arylfervenulins (top) and 3-Aryltioxflavins (bottom).

electron-withdrawing power of a chlorine atom of Ib and then the Faraday B value of Ib becomes larger than the Faraday B value of Ia. The electron migration is interfered by the electron-donating power of a methoxy group of Ic and consequently the Faraday B value of Ic turns out smaller than the Faraday B value of Ia. As the second band of Ia may correspond to the electron migration indicated in (B) of Figure VI, it is expected that the substituent effect on the second band is opposite to the substituent effect on the first band.

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