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Absorption Spectra and Chemical Structure. III. Effects of Substituents and Structure

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RECEIVED JULY 16, 1953

In previous studies a quantitative correlation of $\lambda_{\max}$ with molecular structure for the long wave length absorption band of certain polyenes was made. In this paper the effect of furanoid oxide substituents and of certain spectroscopically effective rings are discussed.

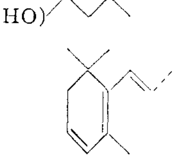
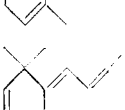
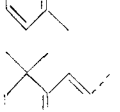
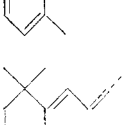
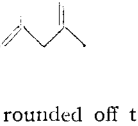
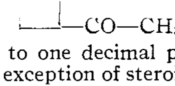
In the preceding paper[1] it was stated that the $\lambda_{\max}$ for the first absorption band of polyenes and its derivatives can be calculated by

$$(\lambda_{\max}^{\text{solv}})^2 = -2.12 + B^{\text{solv}}(1 - 0.920^N) \times 10^4\ \text{m}\mu^2 \quad (1)$$

where B^{solv} is characteristic of the solvent (see Table II, part II), and N is the homoconjugation index, which is defined by the number of conjugated homochromophoric groups and by the number and type of substituents and of spectroscopically effective structures.

TABLE I

RATIOS OF EFFECTS OF SUBSTITUENTS AND STRUCTURES TO THAT OF ETHYLENE CHROMOPHORE

No.	Substituents and structures		Ratio[a]
1	Alkyl substituent[b]	R	+0.13
2		R′	+ .17
3		I	+ .09
4	α-Hydroxyalkyl substituent[c]	A	+ .15
5		A′	+ .11
6	Acyloxy and alkoxyl substituent	AcO RO	+ .00
7	α,β-Epoxyalkyl substituent	Ep	+ .18
8	Furanoid oxide substituent	FO	+ .02
9	Exocyclic ethylene linkage	ex	+ .07
10	Endocyclic ethylene linkage	en	+ .04
11	1,2-Dihydrobenzene structure	db	+ .83
12	1,2,5,6-Tetrahydronaphthalene struct.	tn	+1.12
13		r1	−0.81
14		r2	−0.57
15		r3	−1.04
16		r4	−0.20
17		r5	− .90
18		r6	− .39

[a] Values rounded off to one decimal place are employed for calculation with the exception of steroids and compounds for which $2 \leqq N < 3$. [b] Alkyl substituents include α-acyloxyalkyl, α-alkoxyalkyl and alkyl groups with chromophore in the α-position; for the effect of the alkyl substituent on N, see Table IV, part I. [c] A = substituents in α- or ω-position; A′ = substituents in position other than α or ω.

The spectroscopic effect (*i.e.*, the contribution to N) of various substituents, linkages and rings is summarized in Table I.

It has been known that r2 (Table I) has a hypsochromic effect.[2] N_{r2} was computed from the difference between the observed $\lambda_{\max}$ for compounds 12 and 13 (Table II) and the values calculated without consideration of the hypsochromic effect of r2; $N_{\text{r2}} = -0.57(-0.6)$.

According to Fieser,[1] the hypsochromic effect of r1 and r2 is due to steric hindrance which prevents the ethylene linkage in these rings from becoming sufficiently coplanar with the open-chain polyene; this explanation is also applicable to r3, r4 and r5. The similar unsaturated ring in compound 20, Table II, will not exert a hypsochromic effect, since the ethylene linkage in the ring is not conjugated with those in the open chain; in fact, isoanhydrovitamin A (Table II, 20) shows the simple bathochromic effect ($N_{\text{ex}} = +0.1$) of the exocyclic linkage.

The values for r3 and r4 were determined by the method discussed for r2; $N_{\text{r3}} = -1.0$ and $N_{\text{r4}} = -0.2$.

In view of the many experimental data for compounds containing r2 or r4, and the good agreement between the calculated and observed $\lambda_{\max}$ (except for 11 in alcohol and 15 in cyclohexane (Table II), the above values for N_{r2} and N_{r4} seem to be quite reasonable. The validity of N_{r3} can-

TABLE II

ABSORPTION MAXIMA OF POLYENES WITH SPECIAL SUBSTITUENT OR STRUCTURE (mμ)[a] IN VARIOUS SOLVENTS

No.	Compound	n	R	Other effects	N
1	Aurochrome	7	4	FO:2	7.4
2	Cryptochrome	7	4	FO:2	7.4
3	Auroxanthin	7	4	FO:2	7.4
4	Flavochrome	8	5	FO:1	8.5
5	Flavoxanthin	8	5	FO:1	8.5
6	Chrysanthemaxanthin	8	5	FO:1	8.5
7	Luteochrome	8	4	Ep:1 FO:1	8.6
8	Mutatochrome (citroxanthin)	9	7	FO:1 r1:1	8.9
9	Cryptoflavin	9	7	FO:1 r1:1	8.9
10	Mutatoxanthin	9	7	FO:1 r1:1	8.9
11	Anhydrovitamin A,	6	5	r2·1	5.9
12	Dehydro-β-carotene (isocarotene)	12	10	r2:2	11.8
13	Eschscholzxanthin	12	10	r2:2	11.8
14	Vitamin A_2	6	5	A:1 r3:1	5.6
15	Anhydroeschscholzxanthin	14	10	r4:2	14.6
16	Aphanin	11	10	r1:1 r5:1 (a)	10.3
				(b)	10.9
17	Aphanin oxime	11	10	r1:1 r5:1 (a)	10.3
				(b)	10.9
18	Dihydrorhodoxanthin	11	10	r5:2	10.2
19	Dihydrorhodoxanthin dioxime	11	10	r5:2	10.2
20	Isoanhydrovitamin A	5	4	ex:1	5.5
21	Dihydro-bis-anhydro-β-carotenone	10	8	r6:2	10.0

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(1) K. Hirayama, THIS JOURNAL, **77**, 379 (1955).

(2) L. F. Fieser, *J. Org. Chem.*, **15**, 930 (1950).

TABLE II (*Continued*)

Solvent	Cpd.	Calcd.	Obsd.
Carbon disulfide	1	427	428
	2	427	424
	3	427	423
	4	451	451
	5	451	449
	6	451	449
	7	453	451
	8	458.5	459
	9	458.5	459
	10	458.5	459
	12	504	504
	13	504	502[d]
	15	538	539[d]
	16a	483	494
	16b	491	494
	17a	483	492
	17b	494	492
	18	481	479
	19	481	479
	21	478	478
Cyclohexane	13	478	475[d]
	15	510	503[d]
Chloroform	4	431	433
	5	431	430
	6	431	430
	8	438	438
	9	438	438
	10	438	437
	12	483.5	485
	13	483.5	488[d]
	15	515	516[d]
	16a	462	474
	16b	471	474
	17a	462	472
	17b	471	474
	18	460.5	460
	21	457	459
Hexane	5	419	422[b]
	8	426	427
	15	501.5	500[d]
	18	448	449
	19	447	449
Alcohol	3	398.5	403
	5	421	421
	6	421	421
	9	428.5	430
	10	428.5	427
	11	362	370[c]
	13	473	472[d]
	14	352	352
	18	450	450
	20	350	347
Pyridine	10	444	443
	13	490	489[d]
	16a	468	477
	16b	477	477
	17a	468	477
	17b	477	477
Light ligroin	5	421	422[b]
	16a	452	460
	16b	460	460
	17a	452	459
	17b	460	459
	18	451	452
	19	451	451.5
	21	448	448
Ether	13	473	473[d]
Benzene	4	434	434
	5	434	430
	8	442	440
	9	442	439
	10	442	439
	13	487	486[d]
	16a	464	472
	16b	474	472
	17a	464	472
	17b	474	472
	21	461	460
Methanol	5	417	420[b]
	16a	447	457
	16b	457	457
	17a	447	457
	17b	457	457
Petroleum ether	4	420	422
	5	420	421
	6	420	421
	10	427	426
	12	471	475
	13	471	472[d]

[a] Experimental data: P. Karrer and E. Jucker, "Carotenoids," Elsevier Publishing Co., Inc., Houston, Texas, 1950, unless otherwise indicated. [b] R. Kuhn and H. Brockmann, *Z. physiol. Chem.*, **213**, 192 (1932). [c] P. Karrer and C. H. Eugster, *Helv. Chim. Acta*, **34**, 1805 (1951). [d] P. Karrer and E. Leumann, *ibid.*, **34**, 445 (1951). [e] B. C. L. Weedon and R. J. Woods, *J. Chem. Soc.*, 2687 (1951).

not be discussed at present, as there are no other data.

N_{r5} was computed from the observed values for λ_{max} of compounds 18 and 19 (Table II); the value ($N_{r5} = -0.9$) is very close to that of N_{r1} as expected. However, in the case of compounds 16 and 17, better agreement was obtained with $N_{r5} = -0.3$; therefore the structural formula of either dihydrorhodoxanthin (Table II, 18) or aphanin (Table II, 16), probably the latter, is doubtful.

In the case of the oxide substituents of carotenoids, the α,β-epoxyalkyl group exerts a rather large bathochromic effect, but the effect of the furanoid oxide group (FO), computed from the observed values for λ_{max} of compounds 1–10 (Table II), is almost zero ($N_{FO} = +0.02$).

The ring of dihydro-bis-anhydro-β-carotene (r6, Table I) exerts a hypsochromic effect ($N_{r6} = -0.4$) quite unexpectedly in view of its exocyclic ethylene structure.

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Absorption Spectra and Chemical Structure. IV. Unsaturated Aldehydes, Ketones and Carboxylic Acids

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RECEIVED JULY 16, 1953

The wave length of the first absorption maximum of a conjugated system, with either a carbonyl or carboxyl group at the α-position or at both the α- and ω-positions, also can be expressed by the functional relationship $(\lambda_{max})^2 = A - BC^N$.

The following equations, which are applicable to polyene derivatives, were discussed in the appendix to Part I.

For polyenes with no chromophoric substituents

$$(\lambda_{max})^2 = a + B(1 - C^N) \quad (1)$$
$$= A - BC^N \quad (2)$$

For polyenes with the same chromophoric substituents in α- and ω-positions

$$(\lambda_{max})^2 = a'' + b_{het} + BC_{het}{}^2(1 - C^N) \quad (3)$$
$$= A'' - B''/C^N \quad (4)$$

Similarly for conjugated systems with only one heterochromophore which is in the α-position, the following equations may be applied

$$(\lambda_{max})^2 = a' + \frac{b_{het}}{2} + BC'_{het}{}^2(1 - C^N) \quad (5)$$
$$= A' - B'C^N \quad (6)$$

where a' is the intercept value when $N = 0$, and B and C have the meanings given in previous cases; the value for C used in 2 and 4 should be satisfactory for 6.

For conjugated polyene α-aldehydes, A' and B' were computed from the observed values for λ_{max} in petroleum ether[1] with $C = 0.920$ and substituted in 6 to give

$$(\lambda^{p.e.}_{max})^2 = (39.78 - 39.33 \times 0.920^N) \times 10^4 \text{ m}\mu^2 \quad (7)$$

The values calculated by 7 (Table I, 1–9) show good agreement with the observed values.

Ketones, which can be considered as derivatives of aldehydes in which the hydrogen of the –CHO

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(1) As shown in part II, the λ_{max} of polyenes in hexane, petroleum ether and light ligroin vary only slightly with the solvent; therefore in this part, the same value for B' is used for the calculation of the λ_{max} in these three solvents. Consequently, in many cases the observed values in light ligroin and in hexane are a little longer and a little shorter, respectively, than the corresponding calculated values.