TABLE II (*Continued*)

| 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 $\lambda_{max}$ 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 $\alpha,\beta$-epoxyalkyl group exerts a rather large bathochromic effect, but the effect of the furanoid oxide group (FO), computed from the observed values for $\lambda_{max}$ of compounds 1–10 (Table II), is almost zero ($N_{FO} = +0.02$).

The ring of dihydro-bis-anhydro-$\beta$-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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[CONTRIBUTION FROM INSTITUTE OF POLYTECHNICS, OSAKA CITY UNIVERSITY]

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

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The wave length of the first absorption maximum of a conjugated system, with either a carbonyl or carboxyl group at the $\alpha$-position or at both the $\alpha$- and $\omega$-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.

$$\left.\begin{array}{l}\text{For polyenes with no}\\ \quad\text{chromophoric}\\ \quad\text{substituents}\end{array}\right\} \begin{array}{lr}(\lambda_{max})^2 = a + B(1 - C^N) & (1)\\ \qquad\quad\; = A - BC^N & (2)\end{array}$$

$$\left.\begin{array}{l}\text{For polyenes with}\\ \quad\text{the same}\\ \quad\text{chromophoric}\\ \quad\text{substituents in } \alpha\text{-}\\ \quad\text{and } \omega\text{-positions}\end{array}\right\} \begin{array}{lr}(\lambda_{max})^2 = & \\ a'' + b_{het} + BC_{het}{}^2(1 - C^N) & (3)\\ = A'' - B''/C^N & (4)\end{array}$$

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

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

$$= A' - B'C^N \qquad (6)$$

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

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

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 $\lambda_{max}$ 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 $\lambda_{max}$ 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.

TABLE I

ABSORPTION MAXIMA OF POLYENES WITH ONE CARBONYL OR CARBOXYL SUBSTITUENT IN α-POSITION

| No. | Compound | Subst. and structure[a] $n$ | R | $r_1$ | Ac | N | Solv.[b] | λmax, mμ Obsd.[c] | Calcd. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2,4-Hexadienal | 2 | 1 | 0 | 0 | 2.1 | Hex. | 262[d] | 260 |
| 2 | 2,4,6-Octatrienal | 3 | 1 | 0 | 0 | 3.1 | Hex. | 306[d] | 307 |
| 3 | Retinene$_1$ | 5 | 5 | 1 | 0 | 4.7 | Hex. | 365[e] | 363.5 |
| 4 | α-Apo-2-carotenal | 8 | 5 | 0 | 0 | 8.5 | P.e. | 450[e] | 452 |
| 5 | α-Citraurin | 8 | 5 | 0 | 0 | 8.5 | P.e. | 450 | 452 |
| 6 | β-Apo-2-carotenal | 9 | 7 | 1 | 0 | 8.9 | P.e. | 454 | 459 |
| 7 | β-Citraurin | 9 | 7 | 1 | 0 | 8.9 | Hex. | 458 | 459 |
| 8 | Apo-3-lycopenal | 9 | 6 | 0 | 0 | 9.6 | L.l. | 473 | 470 |
| 9 | Apo-2-lycopenal | 10 | 6 | 0 | 0 | 10.6 | L.l. | 490.5 | 385 |
| 10 | 3,5-Heptadien-2-one | 2 | 1 | 0 | 0 | 2.1 | Hex. | 264[d] | 260 |
| 11 | Dihydroxysemi-β-carotenone | 9 | 5 | 0 | 0 | 9.5 | P e. | 468 | 469 |
| 12 | *t*-Butyl β-apo-1-carotenyl ketone | 10 | 7 | 1 | 0 | 9.9 | P.e. | 473 | 474 |
| 13 | Capsanthin | 10 | 7 | 1 | 0 | 9.9 | L.l. | 475 | 474 |
| 14 | Capsanthin dipalmitate | 10 | 7 | 1 | 0 | 9.9 | P.e. | 473 | 474 |
| 15 | Semi-β-carotenone | 10 | 7 | 1 | 0 | 9.9 | P.e. | 470 | 474 |
| 16 | 2,4,6-Octatrien-1-oic acid | 3 | 1 | 0 | 1 | 2.8 | Hex. | 302[d] | 294 |
| 17 | 3-Methyl-2,4,6-octatrien-1-oic acid | 3 | 2 | 0 | 1 | 2.9 | Hex. | 296[d] | 298 |
| 18 | 2,4,6,8-Decatetraen-1-oic acid | 4 | 1 | 0 | 1 | 3.8 | Hex. | 330[d] | 334 |
| 19 | Methylazafrin | 7 | 4 | 0 | 1 | 7.1 | L.l. | 422.5 | 424 |
| 20 | Torularhodin | 12 | 8 | 1 | 1 | 11.7 | L.l. | 501 | 499.5 |
| 21 | Torularhodin methyl ester | 12 | 8 | 1 | 1 | 11.7 | L.l. | 498 | 499.5 |

[a] R = number of alkyl substituents; $r_1$ = number of conjugated rings $r_1$ (see Table I, part III); Ac = number of carboxyl groups in α-position. [b] Hex. = hexane; p.e. = petroleum ether; l.l. = light ligroin. [c] Experimental data, unless otherwise indicated, from P. Karrer and E. Jucker. "Carotenoids," Elsevier Publishing Co., Inc., Houston, Texas, 1950. [d] K. Dimroth, *Angew. Chem.*, **52**, 545 (1939). [e] L. F. Fieser, *J. Org. Chem.*, **15**, 930 (1950).

TABLE II

ABSORPTION MAXIMA OF POLYENES WITH CARBONYL OR CARBOXYL GROUPS AT α- AND ω-POSITIONS

| No. | Compound | Subst. and structure[a] $n$ | R | Ac | $N$ | Solv.[b] | λmax, mμ Obsd.[c] | Calcd. |
|---|---|---|---|---|---|---|---|---|
| 1 | Apo-3,12-lycopenedial | 8 | 4 | 0 | 8.4 | P.e. | 452 | 453 |
| 2 | Apo-2,12-lycopenedial | 9 | 4 | 0 | 9.4 | P.e. | 468 | 468 |
| 3 | β-Carotenone aldehyde | 7 | 3 | 0 | 7.3 | Hex. | 431 | 434 |
| 4 | 4-Hydroxy-β-carotenone aldehyde | 7 | 3 | 0 | 7.3 | Hex. | 433 | 434 |
| 5 | Capsylaldehyde | 7 | 3 | 0 | 7.3 | Hex. | 431 | 434 |
| 6 | Capsanthylal | 8 | 4 | 0 | 8.4 | P.e. | 452 | 453 |
| 7 | Apo-2-norbixinal methyl ester | 7 | 3 | 1 | 7.0 | P.e. | 424 | 428 |
| 8 | Apo-1-norbixinal methyl ester | 8 | 4 | 1 | 8.1 | P.e. | 445 | 448 |
| 9 | β-Carotenone | 9 | 4 | 0 | 9.4 | Hex. | 466 | 467.5 |
| 10 | Physallienone | 9 | 4 | 0 | 9.4 | P.e. | 464 | 467.5 |
| 11 | Capsorubin | 9 | 4 | 0 | 9.4 | L.l. | 474 | 467.5 |
| 12 | Capsorubin dipalmitate | 9 | 4 | 0 | 9.4 | Hex. | 474 | 467.5 |
| 13 | Capsanthinone | 9 | 4 | 0 | 9.4 | Hex. | 472 | 467.5 |
| 14 | Azafrinone | 7 | 3 | 1 | 7.0 | L.l. | 429 | 430 |
| 15 | Methylazafrinone | 7 | 3 | 1 | 7.0 | L.l. | 429 | 430 |
| 16 | Crocetin | 7 | 4 | 2 | 6.8 | L.l. | 424.5 | 424.5 |
| 17 | Crocetin dimethyl ester | 7 | 4 | 2 | 6.8 | L.l. | 424.5 | 424.5 |
| 18 | Methylbixin | 9 | 4 | 2 | 8.8 | Hex. | 450 | 459 |

[a] See *a*, Table I. [b] See *b*, Table I. [c] Experimental data from P. Karrer and E. Jucker, "Carotenoids," Elsevier Publishing Co., Inc., Houston, Texas, 1950.

chromophore is substituted by an alkyl auxochrome, show a slight bathochromic effect in petroleum ether; however this effect is negligible in comparison to that of the ethylene chromophore (about 4%), and equation 7 can be used without modification for α-keto conjugated polyenes. The examples given in Table I (10–15) show good agreement.

On the other hand, carboxylic acids, in which the hydrogen of the –CHO chromophore is replaced by an –OH auxochrome, show a marked hypsochromic effect in petroleum ether, about 30% of the bathochromic effect of the ethylene chromophore. Therefore, the $\lambda_{\max}$ of conjugated polyene α-carboxylic acids may be calculated by 7 if $N_{\text{acid}} = -0.3$ is taken into consideration[2]; actually the calculated values in Table I (16–21) agree well with the observed.[3]

Now, $a$, $a''$ and $a'$ in equations 1, 3 and 5, respectively, are compensatory terms, representing partial effects which do not change in progression, and there exists an approximate relationship between them, $2a' = a + a''$. Thus

$$2(a' + b_{\text{het}}/2) = a + (a'' + b_{\text{het}}) \qquad (8)$$

and for polyene α,ω-dialdehydes

$$a'' + b_{\text{het}} = 3.02$$

which is obtained by substituting $a = -2.12$ found for polyenes and $a' + b_{\text{het}}/2 = 0.45$ for polyene-α-aldehydes (see equation 7) in equation 8. From these data and the observed values, the parameter $B''$ was calculated to be 34.67. Thus

$$(\lambda_{\max}^{\text{p.e.}})^2 = (37.69 - 34.67 \times 0.920^N) \times 10^4\ \text{m}\mu^2 \qquad (9)$$

is the equation for polyene α,ω-dialdehydes (Table II, 1 and 2); the same equation is also applicable to α-keto-ω-aldehydes (II, 3–6) and to α,ω-diketones (II, 9–13). Equation 9 also can be used for α-aldehyde-ω-carboxylic acids (II, 7 and 8), α-keto-ω-carboxylic acids (II, 14 and 15) and α,ω-dicarboxylic acid (II, 16–18), with $N_{\text{acid}} = -0.3$ as previously determined.

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(2) –CHO → –COR or –COOH cannot be regarded as simple auxochromic substitution, such as =CH— → =CR—, because in the former auxochromic substitution occurs not in the homochromophore, but in the heterochromophore. As there are insufficient data for the exact computation of parameters $A'$ and $B'$ (or $A''$ and $B''$), we assume that the homoconjugation method is applicable to these cases and that the change occurs in $N$.

(3) The method of calculation of $N$ and $\lambda_{\max}$ is illustrated in part II.