

### THE STRUCTURE OF KRYPTOCAPSIN

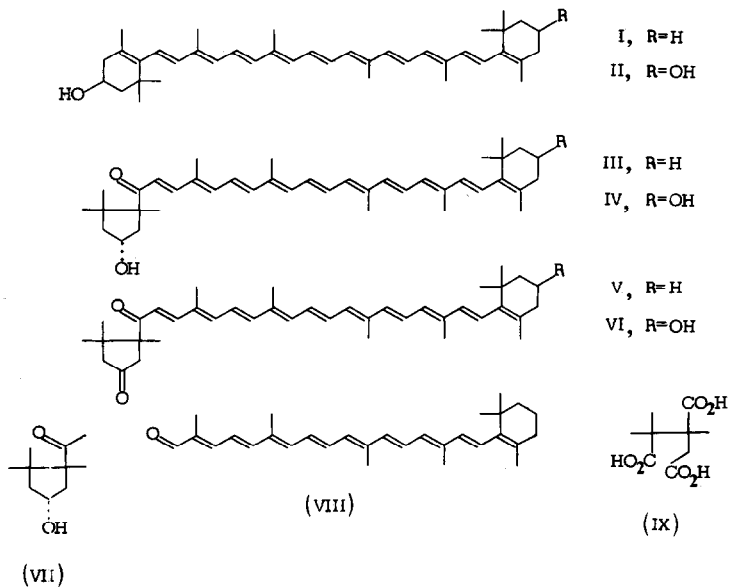
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Kryptocapsin, a minor constituent of the mixture of carotenoids present in Capsicum annum, is related biogenetically to kryptoxanthin (I) via the mono-epoxide in the same way that capsanthin is related to zeaxanthin (II).<sup>1</sup> Following the elucidation of the structure of capsanthin (IV),<sup>2-4</sup> kryptocapsin was tentatively formulated as (III).<sup>2</sup> This structure has now been confirmed.

Kryptocapsin,  $C_{40}H_{56}O_2$ , m.p. 160-161°, has light absorption\* ( $\lambda_{max}$ . 520 (inflection) and 486 m $\mu$ ,  $\epsilon \times 10^{-3} = 87$  and 112 respectively;  $\nu_{max}$ . 1664, 1582 and 971  $cm^{-1}$ ) and nuclear magnetic resonance spectra ( $\tau_{CDCl_3}$  9.16, 8.97, 8.80, 8.65, 8.29 and 8.02; relative intensities 1:2:1:1:1:4 respectively) which are very similar to those of capsanthin,<sup>2</sup> and provide strong evidence for the decaeneone chromophore and for the 2,6,6-trimethylcyclohexenyl- and trans-3-hydroxy-1,5,5-trimethylcyclopentyl-ring systems. Support for the location of the hydroxyl group is provided by chromic acid oxidation of kryptocapsin to camphoronic acid (IX) (identified by paper chromatography),<sup>5</sup> and by Oppenauer oxidation

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\* Visible and infra-red light absorption spectra were determined in benzene and chloroform respectively.



to a cyclopentanone, "kryptocapsone" (V),  $C_{40}H_{54}O_2$ , m.p. 171-172°, which has light absorption ( $\lambda_{max}$ . 491 m $\mu$ ,  $\epsilon \times 10^{-3} = 108$ ;  $\nu_{max}$ . 1739 and 1661  $cm^{-1}$ ) and n.m.r. properties ( $\tau_{CDCl_3}$  9.02 (shoulder), 8.99, 8.78, 8.64, 8.31 and 8.06; relative intensities ca. 1:2:1:1:4 respectively) resembling those of capsanthone (VI).<sup>2</sup> On treatment with aqueous alcoholic potassium hydroxide kryptocapsin undergoes a retro-aldol cleavage to give  $\beta$ -apo-2-carotenal (VIII) (mixed chromatogram with an authentic specimen). Reduction of kryptocapsin with lithium aluminium hydride, followed by treatment of the resulting "kryptocapsol" ( $\lambda_{max}$ . 487, 457 and 432 m $\mu$ ,  $\epsilon \times 10^{-3} = 116, 128$  and 87 respectively) with hydrogen chloride in chloroform, gives "anhydro-kryptocapsol" ( $\lambda_{max}$ . 498, 466 and 440 m $\mu$ ,  $\epsilon \times 10^{-3} = 84, 108$  and 81 respectively); in contrast capsanthin,

which has a hydroxyl group in the six-membered ring, gives bisanhydrocapsanthol ( $\lambda_{\text{max.}}$  522, 489 and 461  $\mu$ ,  $\epsilon \times 10^{-3} = 112, 135$  and 96 respectively).<sup>6</sup> Finally, condensation of  $\beta$ -apo-2-carotenal (VIII)<sup>7</sup> with (VII)<sup>4</sup> in the presence of alcoholic potassium hydroxide gives ( $\pm$ )-kryptocapsin, m.p. 131-132<sup>o</sup>;  $\lambda_{\text{max.}}$  520 (inflexion) and 486  $\mu$ ,  $\epsilon \times 10^{-3} = 93.7$  and 115 respectively;  $\nu_{\text{max.}}$  3650, 1660, 1585 and 970  $\text{cm}^{-1}$ ;  $\tau_{\text{CHCl}_3}$  9.15, 8.97, 8.80, 8.63, 8.28 and 8.02, relative intensities 1:2:1:1:1:4 respectively. This does not separate from the natural pigment on thin layer chromatography (Kieselgel; eluent 2% acetone in light petroleum, b.p. 60-80<sup>o</sup>;  $R_F = 0.47$ ). There is little doubt that the absolute configuration of the cyclopentyl ring in kryptocapsin is the same as that in capsanthin.<sup>8</sup>

Full details of the above degradative and synthetic evidence will be published separately by the Hungarian and British authors respectively.

## REFERENCES

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- <sup>4</sup> R.D.G. Cooper, L.M. Jackman and B.C.L. Weedon, Proc. Chem. Soc. 215 (1962).
- <sup>5</sup> cf. L. Cholnoky and J. Szabolcs, Experientia 16, 483 (1960).
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