On the Crystal Structure of Carotenoids

BY G. MACKINNEY

In Table I are listed x-ray powder patterns of various carotenoid preparations. Though describing no patterns, Karrer and co-workers[1] state that no differences were detectable between carotene, xanthophyll, and lutein. Such results may be caused by oxidation, as powdered xanthophylls in particular are unstable, and should be exposed *in vacuo*. Patterns were obtained by exposure *in vacuo* of powdered crystalline material to the Kα radiation of molybdenum.

TABLE I

INTERPLANAR SPACINGS IN ÅNGSTRÖM UNITS

I, Carotene

a, Carrot roots 1. $CHCl_3$–pet. ether	2. CS_2–EtOH	b, Spinach[a] cauliflower[a] sunflower leaves 1. $CHCl_3$–EtOH
7.53 w	7.50 w	7.51 w
6.04 s	5.96 s	6.10 s
5.70 s	5.68 s	5.73 s
5.28 w	5.31 w	5.27 w
..	5.00 w	5.02 w
4.69 w	4.67 w	4.70 w
..	4.40 w	4.41 w
4.07 s	4.04 s	4.08 s
3.77 w	3.81 w	3.79 w
3.60 s	3.60 s	3.59 s
..	..	3.33 vw
3.02 vw	..	3.01 vw

II, Leaf Xanthophyll		III, Lutein	IV, Lycopene[a]
a, MeOH[a]	b, $CHCl_3$–pet. ether	CH_2Cl_2–*n* heptane	CS_2–EtOH
6.60 m	6.55 s	6.70 m	
..	..	6.00 w	5.79 s
5.51 m	5.40 m	5.50 m	5.27 s
5.10 w	4.95 w	5.00 w	4.90 s
4.61 w	4.5–4.2 band	4.40–4.15 band	..
3.91 s	4.05 s	4.08 s	4.14 w
3.70 m	..	3.80 m	3.97 s
3.53 s	3.65 s	3.66 s	3.62 s
		3.30 w	3.43 s
			3.18 vw
			3.00 vw

[a] Samples provided by courtesy of Dr. James H. C. Smith. s = strong, w = weak, etc.

The carotenes, from carrot roots and the leaves of spinach, cauliflower and sunflower, were variously recrystallized with EtOH and petroleum ether from CS_2 and $CHCl_3$. Xanthophyll, from sunflower leaves, was recrystallized from MeOH, and from $CHCl_3$–petroleum ether. Lutein was isolated from its ester, helenien, in sunflower petals and precipitated from CH_2Cl_2–*n*-heptane. Lycopene, from tomatoes, was recrystallized from CS_2–EtOH.

(1) Karrer, *et al.*, *Helv. Chim. Acta*, **14**, 614 (1931).

No spacings longer than 7.53 Å. were observed, though the range explored would have recorded up to 15 Å. One may estimate that no first order reflections have been photographed. Spacings longer than 6.0 Å. were measured within ±0.05 Å., and the error falls rapidly with increase in the angle of reflection.

The similarity of the carotene preparations is noteworthy. With no significant variation in pattern, it seems improbable that carotene takes up ethanol of crystallization. Between lutein and leaf xanthophyll, there is no significant difference. In the samples used, $[\alpha]^{20}_{6678}$ for lutein was +128° (25.8 mg. in 15 cc. of $CHCl_3$) and for xanthophyll, +107° (7.0 mg. in 15 cc. of $CHCl_3$). The latter is probably a mixture containing chiefly lutein.

Certain similar interplanar spacings suggest many common structural features in these large carotenoid molecules, but definite differences, both of spacing and intensity, are to be noted in the x-ray diffraction powder patterns of carotene, leaf xanthophyll and lutein, and lycopene.

Acknowledgment is made to Professor W. H. Dore, of the University of California, with whom this work was performed.

CARNEGIE INSTITUTION OF WASHINGTON
DIVISION OF PLANT BIOLOGY
STANFORD UNIVERSITY, CAL.

RECEIVED NOVEMBER 20, 1933

Elementary Organic Reactions

BY F. O. RICE

In connection with the work in this Laboratory on the decomposition of organic compounds through a free radical mechanism,[1] it has been necessary to assume definite values for the activation energies of a number of simple organic reactions. It seems desirable to list these reactions together with the activation energies assigned and discuss briefly the somewhat conflicting evidence available.

(1)	$H + CH_4 \longrightarrow H_2 + CH_3$	> 20
(3)	$H + C_2H_6 \longrightarrow H_2 + CH_3CH_2$	17
(5)	$CH_3 + H_2 \longrightarrow CH_4 + H$	23
(7)	$CH_3CH_2 + H_2 \longrightarrow C_2H_6 + H$	25
(9)	$CH_3 + C_2H_6 \longrightarrow CH_4 + CH_3CH_2$	20
(11)	$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2$	15
(13)	$CH_3 + CH_3OCH_3 \longrightarrow CH_4 + CH_3OCH_2$	15
(15)	$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO$	15
(2)	$CH_4 \longrightarrow CH_3 + H$	100

(1) Rice, THIS JOURNAL, **53**, 1959 (1931); Rice and Herzfeld, *ibid.*, **56**, 284 (1934).