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Some Poly-*cis*-lycopenes Occurring in the Fruit of *Pyracantha*

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In the course of recent investigations it has been found that mixtures of *cis-trans* isomers of carotenoids can be obtained by several laboratory methods and that they mainly contain mono- and di-*cis* isomers besides the unchanged portion of the all-*trans* form.[1] It has not been possible so far to prepare *in vitro* such poly-*cis* carotenoids which contain most or all of the sterically available double bonds in *cis* position. It was, therefore, a welcome extension of the experimental possibilities that two poly-*cis* carotenoids, prolycopene,[2] $C_{40}H_{56}$, and pro-γ-carotene,[3] $C_{40}H_{56}$, were found to occur in the vegetable kingdom, and could be isolated in crystalline, pure state. That other stereoisomeric pigments of a similar type are also present in some extracts follows from earlier reports.[2,3]

Since it was desirable to test some theoretical interpretations and viewpoints on as many well-defined poly-*cis* carotenoids as possible, a detailed fractionation of the pigment which develops during the ripening of the berries of *Pyracantha angustifolia* Schneid. was undertaken. A first investigation of this fruit was reported in collaboration with Schroeder,[2] and the influence of the ripening process on the composition of the polyene mixture was reported by Sandoval and one of the authors.[4]

As described in the Experimental Part, the *Pyracantha* pigment consists almost entirely of hydrocarbon-carotenoids[2] whose complicated mixture includes representatives of the α-carotene, β-carotene, γ-carotene and lycopene sets (Table I). One well-known stereoisomer of β-carotene, neo-β-carotene U, appeared in the chromatograms of each crude extract; however, its occurrence in the berries cannot be strictly proved. In contrast, a new, well-crystallized stereoisomer of γ-carotene, termed neo-γ-carotene P, can be claimed as a genuine plant constituent since it does not occur in detectable quantity if all-*trans*-γ-carotene is isomerized *in vitro*.

The *Pyracantha* fruit offers a considerable number of stereoisomeric lycopenes (Table I). Besides a limited amount of the all-*trans* form (for example, 14 mg. in a kilo of fresh berries) and a relatively large quantity of prolycopene, six new isomers were found and termed poly-*cis*-lycopenes I to VI in the order of their decreasing adsorbabilities

TABLE I

CHROMATOGRAPHIC SEQUENCE OF SOME POLYENE HYDROCARBONS ISOLATED FROM *Pyracantha* BERRIES

(Calcium Hydroxide; Petroleum Ether and 0 to 8% Acetone. The figures denote amounts isolated in crystals per 1 kg. of fresh berries.)

	Mg.	
Poly-*cis*-lycopene I	3	(top)
Poly-*cis*-lycopene II	0.8	
Poly-*cis*-lycopene III	1.2	
All-*trans*-γ-carotene	3	
Neo-γ-carotene P	3	
Prolycopene	46	
Poly-*cis*-lycopene IV		
Poly-*cis*-lycopene V		
Poly-*cis*-lycopene VI		
Pro-γ-carotene	13	(bottom)

(from petroleum ether solutions on lime). The chromatographically homogeneous pigments IV, V and VI have been observed only in solution because of their very small quantities. On the other hand, the poly-*cis*-lycopenes I, II and III were isolated in the form of analytically pure crystals (Fig. 1). We believe that they are true constituents of *Pyracantha* and cannot have been formed *in vitro* from prolycopene, considering the thermostability of the latter. The poly-*cis*-lycopenes I, II and III themselves are thermostable. When solutions in petroleum ether were refluxed in the dark under carbon dioxide for half an hour, a subsequent chromatogram showed that only traces of other isomers had been formed; the spectral curves likewise were essentially unaltered.

The new poly-*cis*-lycopenes were accepted as such on the following basis. Each shows in the visual spectroscope uncharacteristic, rather blurred bands or shadowed areas without distinct bands. Upon iodine addition in the spectroscopic cell, the well-known bands (502, 471, 441.5 mμ, in petroleum ether) of the stereoisomeric lycopene equilibrium mixture appeared almost instantaneously, with a spectacular increase in intensity and sharpness. The main zone of a subsequent chromatogram did not separate from tomato lycopene in the mixed chromatogram test. Furthermore, each of the six extinction curves taken in the Beckman spectrophotometer after iodine catalysis proved to be practically identical with that taken after iodine addition to all-*trans*-lycopene.

The following results were obtained by the spectrophotometric investigation of the poly-*cis*-lycopenes mentioned (Figs. 2–6 and Table III).

It is safe to assume on the basis of earlier studies[1,2] that each *trans* → *cis* shift involves a certain decrease in the wave length of the maximum of the fundamental band. Although no strict pro-

(1) *Cf.* L. Zechmeister, *Chem. Rev.*, **34**, 267 (1944).

(2) L. Zechmeister, A. L. LeRosen, F. W. Went, and L. Pauling, *Proc. Natl. Acad. Sci.*, **27**, 468 (1941); A. L. LeRosen and L. Zechmeister, THIS JOURNAL, **64**, 1075 (1942); L. Zechmeister and W. A. Schroeder, *J. Biol. Chem.*, **144**, 315 (1942); L. Zechmeister and R. B. Escue, *ibid.*, **144**, 321 (1942).

(3) L. Zechmeister and W. A. Schroeder, THIS JOURNAL, **64**, 1173 (1942).

(4) L. Zechmeister and A. Sandoval, *Arch. Biochem.*, **3**, 425 (1945).

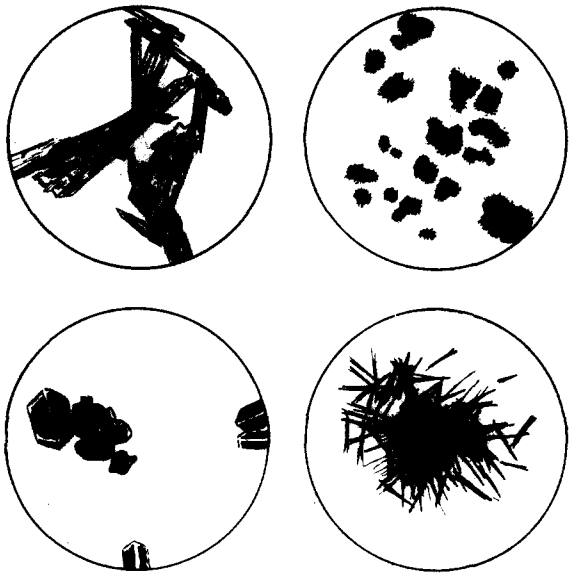

Fig. 1.—Crystal drawings of prolycopene (upper left), poly-*cis*-lycopene I (upper right), poly-*cis*-lycopene II (lower left), and poly-*cis*-lycopene III (lower right). Poly-*cis*-lycopene II was crystallized from petroleum ether and methanol; the others from benzene and methanol. Magnification 430×.

portionality can be expected between this effect and the number of *trans* → *cis* steps, the difference in the position of $\lambda_{max.}$ between a stereoisomer and the corresponding all-*trans* form will give a rough indication of the number of the *cis* double bonds present. According to Table II the poly-*cis*-lycopenes from *Pyracantha* possess four to seven such bonds in the *cis* configuration out of seven sterically unhindered double bonds.

TABLE II

PROBABLE NUMBER OF *cis* DOUBLE BONDS OF SOME STEREOISOMERIC LYCOPENES, BASED ON EXTINCTION DATA IN HEXANE

(The pigments are listed in the sequence of decreasing wave lengths of $\lambda_{max.}$ and increasing number of *cis* double bonds.)

	$\lambda_{max.}$ (mμ)	Diff. in $\lambda_{max.}$ from the all-*trans* form (Beckman spectrophotometer) (mμ)	$E^{mol.}_{1 cm.} \times 10^{-4}$ at $\lambda_{max.}$	Relative extinction areas between 320 and 560 mμ	Probable number of *cis* double bonds present
All-*trans*	472–473	0	18.6	100	0
Neo A	465	7.5	12.2	82	1
Poly-*cis* I	444–445	28	12.3	76	4–5
Poly-*cis* III	444–445	28	11.3	71	4–5
Poly-*cis* II	441	31.5	11.4	70	4–5
Prolycopene	438	34.5	10.3	60	5–6
Poly-*cis* VI	433	39.5	8.1	54	6
Poly-*cis* V	431–432	41	9.0	52	6
Poly-*cis* IV	426	46.5	10.4	62	6–7

It was observed in an early stage of these investigations[5] that all stereoisomeric forms show a decreased color intensity compared with that

(5) L. Zechmeister and P. Tuzson. *Ber.*, **72**, 1340 (1939).

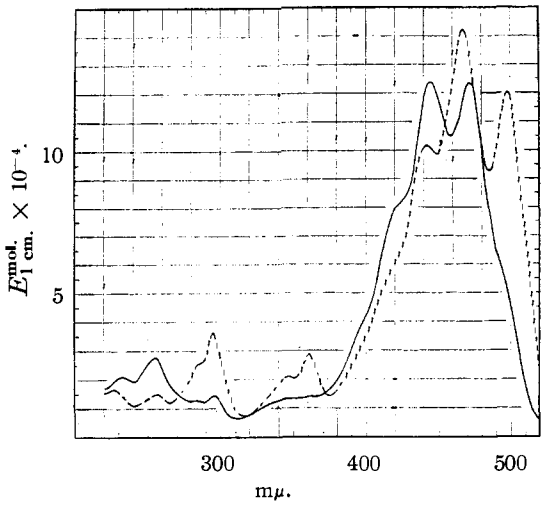

Fig. 2.—Molecular extinction curves of poly-*cis*-lycopene I in hexane: ———, fresh solution: – – – –, after iodine catalysis, in light.

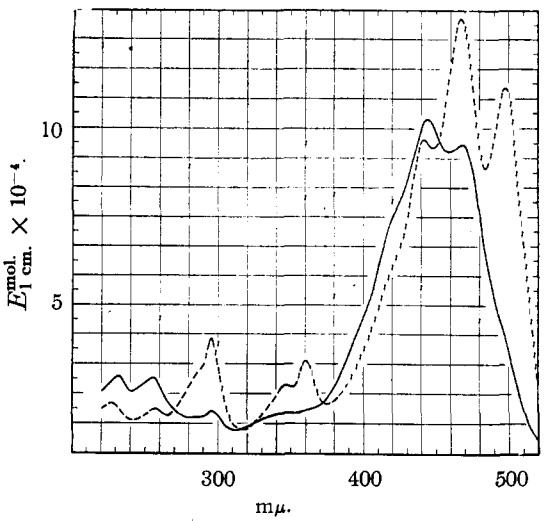

Fig. 3.—Molecular extinction curves of poly-*cis*-lycopene II in hexane: ———, fresh solution; – – – –, after iodine catalysis, in light.

TABLE III

MOLECULAR EXTINCTION COEFFICIENTS OF SOME POLY-*cis*-LYCOPENES AT THEIR MAIN MAXIMA (IN HEXANE)

	Wave length (mμ)	$E^{mol.}_{1 cm.} \times 10^{-4}$
Poly-*cis*-lycopene I	472	12.3
	444–445	12.3
Poly-*cis*-lycopene II	465–466	10.6
	441–442	11.1
Poly-*cis*-lycopene III	468	10.5
	443–446	11.3
Poly-*cis*-lycopene IV	426	10.6
	406	9.0 (7)
Poly-*cis*-lycopene V	431–432	8.9 (8)
	412–414	8.1 (3)
Poly-*cis*-lycopene VI	433	8.1 (6)

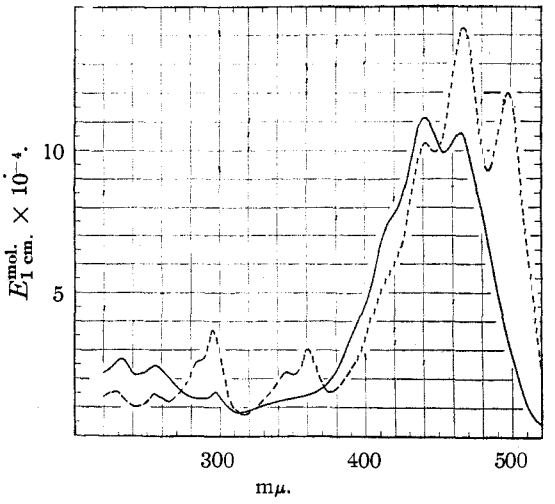

Fig. 4.—Molecular extinction curves of poly-*cis*-lycopene III in hexane: ———, fresh solution; – – – –, after iodine catalysis, in light.

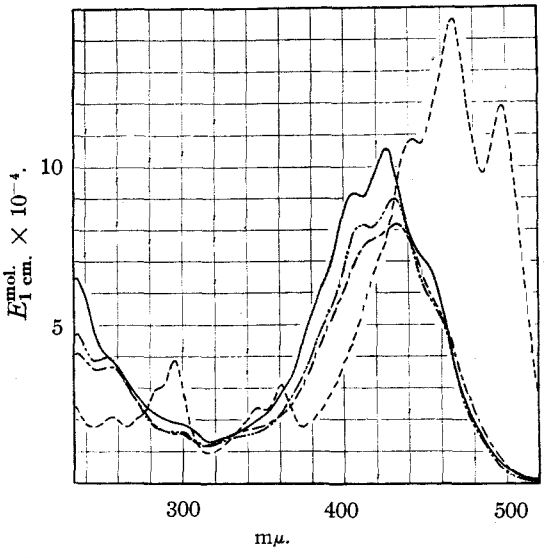

Fig. 5.—Molecular extinction curves of poly-*cis*-lycopenes IV, V and VI in hexane: ———, fresh solution of IV; — – — –, fresh solution of V; — – —, fresh solution of VI; – – – –, after iodine catalysis of V, in light (the peak of IV near 230 mμ requires further confirmation).

TABLE IV

ANALYTICAL DATA FOUND FOR SOME POLYENE HYDROCARBONS FROM *Pyracantha* (CALCD. FOR $C_{40}H_{56}$: C, 89.48; H, 10.52)

	Carbon, %		Hydrogen, %	
Prolycopene	89.02	89.62	10.67	10.87
Poly-*cis*-lycopene I	89.04[a]	89.11	10.56[a]	11.03
Poly-*cis*-lycopene II	89.34		10.55	
Poly-*cis*-lycopene III	89.76	89.49	10.59	10.58
All-*trans*-γ-carotene	89.20[a]	89.49	11.01[a]	10.58
Neo-γ-carotene P	89.18		10.57	
Pro-γ-carotene	89.56		10.92	

[a] These values are corrected for about 1% ash.

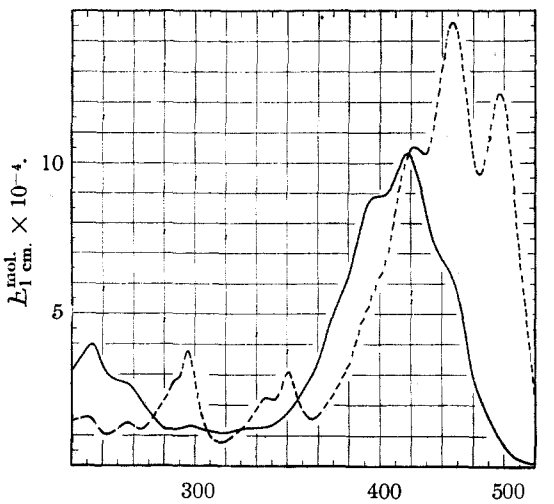

Fig. 6.—Molecular extinction curves of prolycopene in hexane: ———, fresh solution; – – – –, after iodine catalysis, in light.

of the all-*trans* isomer, which, according to Pauling,[6] is in good agreement with theoretical considerations.

The stepwise decrease of the extinction as a function of an increasing number of *cis* double bonds present is demonstrated simply by the color of adsorbates using identical amounts of the respective pigments adsorbed from petroleum ether on lime. The zone of all-*trans*-lycopene is intensely red, that of prolycopene is dull orange while the poly-*cis*-lycopenes V and VI form yellow zones.

For prolycopene the value; $E^{mol.}_{1\,cm.} = 10.3 \times 10^4$ as reported in collaboration with LeRosen, Schroeder, Polgár and Pauling[7] is about 45% lower than the corresponding value for the all-*trans* form (18.6×10^4). Similarly depressed extinctions were observed for all six new poly-*cis*-lycopenes (Table II). These relations are also demonstrated by the respective extinction areas of the fundamental bands (Table II).

Another typical feature of most all-*trans* → *cis* transitions is a decrease of the fine structure in the fundamental band. Border cases in which such a flattening of the curve is not manifest and in which the fundamental band decreased in height without marked alteration in detail have been found so far[8] only in the peripheral-mono-*cis* compounds, neo-α-carotene U and neo-β-carotene U. The loss in fine structure can be characterized for the central mono-*cis*-lycopene, termed neolycopene A, by the extinction ratios, main maximum:minimum:maximum = 1.77:1:1.45 while the corresponding data for all-*trans*-lycopene are 1.86:

(6) L. Pauling, *Fortschr. Chem. org. Naturstoffe*, **3**, 203 (1939).

(7) L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgár and L. Pauling, THIS JOURNAL, **65**, 1940 (1943).

(8) L. Zechmeister and A. Polgár, *ibid.*, **66**, 137 (1944) and **65**, 1522 (1943).

1:1.72. Figures 2–6 demonstrate a far-reaching disappearance of the fine structure. For example the ratios for poly-*cis*-lycopene II are 1.12:1:1.07. There is scarcely an indication of a fine structure left in the curve of poly-*cis*-lycopene VI (Fig. 5).

An inspection of the seventy-two stereoisomeric models shows that most tri-*cis*, tetra-*cis*, penta-*cis* and hexa-*cis* forms of lycopene are characterized by a roughly linear shape of their molecules. A similar shape is shown, for example, by peripheral mono-*cis* and, furthermore, by those models which have two adjacent *cis* double bonds in the center of the chromophore (Fig. 7). In all these cases a flat course of the extinction curve in the *cis*-peak region, *i. e.*, between 320 and 380 mμ, can be expected. This postulate has now been fulfilled by all seven poly-*cis*-lycopenes known (including prolycopene) which contain four to seven *cis* double bonds (Figs. 2–6).

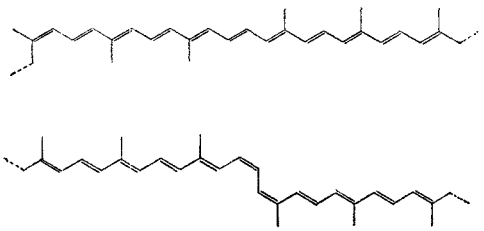

Fig. 7.—Skeleton models of 1-mono-*cis*-lycopene and 6,7-di-*cis*-lycopene.

With reference to the relative adsorption affinities of the stereoisomers the following statement can be made at the present time.

It was reported earlier that the mono-*cis* compound, neolycopene A, shows a moderate decrease in adsorption affinity when compared with the all-*trans* pigment on a lime column. A considerably greater decrease is caused by the presence of several *cis* double bonds. Furthermore, the adsorbabilities of the individual poly-*cis* compounds differ from each other much less than the average adsorbability in this subclass of stereoisomers from that of the all-*trans* form. One can roughly say that the adsorbabilities decrease in the same order as the extinction values of the fundamental bands. Figure 8 which demonstrates the position and shape of the top section of the respective fundamental bands gives in a sense also a demonstration of the chromatographic sequence, from top to bottom.

It is known that *trans* → *cis* shifts may either increase or decrease the adsorption affinity of all-*trans*-α- as well as all-*trans*-β-carotene. Although no lycopene stereoisomer is known which is retained above all-*trans*-lycopene on the Tswett column, we believe that a weakening of adsorbability caused by the presence of many *cis* double bonds would overrule any effect on adsorbability of a single *trans* → *cis* rotation. Considering the similarity in the over-all shape of the all-*trans*-lycopene molecule and some of its poly-*cis* isomers, it is evident that the rod-like form alone is not responsible for the weakening of the adsorption in the subclass of the poly-*cis* lycopenes.

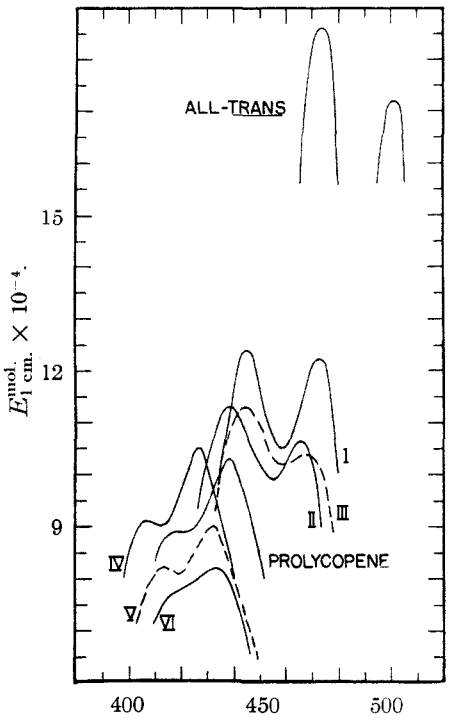

Fig. 8.—Molecular extinction curves of all-*trans*-lycopene, prolycopene and poly-*cis*-lycopenes I–VI at their main maxima, in hexane.

It will require further study before definite configurations can be assigned to the poly-*cis*-lycopenes. More extended experimental data are also necessary in order to make precise statements concerning the interdependence of spectral characteristics, adsorption affinity and stereochemical configuration.

Acknowledgment.—We wish to thank Professor A. J. Haagen-Smit as well as Dr. G. Oppenheimer and Mr. G. Swinehart for micro-estimations; furthermore Mr. M. Gschwind of the Huntington Botanical Gardens for assistance.

Experimental

Materials and Methods.—The adsorbent was calcium hydroxide (Shell Brand Lime, Chemical Hydrate, 98% through 325 mesh, Westvaco Chlorine Products, Newark, Calif., or Sierra Hydrated Lime, United States Lime Products Corp., Los Angeles, Calif.) mixed with 20% celite. The petroleum ether was Skellysolve B, b. p. 60–70°. For the separation of extracts from the ground berries a basket centrifuge was used (diameter, 20 cm.; lined with cloth; International Centrifuge, type SB, size 2). Elutions were carried out in sintered glass funnels with alcohol and the eluates were washed alcohol-free. Evaporations and concentrations took place in a slow stream of carbon dioxide. Crystallizations were carried out by dissolving residues in warm benzene, transferring to centrifuge tubes and adding absolute methanol; recrystallizations, washing and drying were performed in

the same tube to avoid losses. Melting points (cor.) were taken in sealed capillary tubes filled with carbon dioxide in an electrically heated Berl block. For analytical purposes the samples were dried in an Abderhalden apparatus under 0.1 mm. pressure at refluxing acetone temperature for two hours.

For the purpose of catalytic stereoisomerization, iodine (1% of the pigment weight) was added to the hexane solution, in a 10 or 25-ml. glass volumetric flask, whereupon a fifteen-minute illumination followed by means of two 3500° white Mazda lamps (40-watt, length of the tubes 120 cm.; from 60 cm. distance).

Visual spectra were observed in an Evaluating Grating Spectroscope (Zeiss, with light filter BG-7). After the position of the maxima had been determined, a few drops of iodine solution (2–5 μg) were added and the readings repeated after a few minutes. Absorption spectra were taken in hexane (Eastman Kodak Co. practical "hexane," purified with fuming sulfuric acid) in a Beckman photoelectric spectrophotometer. The extinction data are based on estimations using at least two independently weighed samples. For analytical data of the pure samples, *cf.* Table IV.

Extraction.—Fresh *Pyracantha* berries, picked in Southern California, in December and January, were stored under methanol in darkness at 4° until they were worked up. It was found that under these conditions even half a year of storage would not essentially alter the results. Sixteen kilograms of this material (fresh weight) was drained of methanol and the moist berries were coarsely cut in an electric chopper. The material, after having been kept under fresh methanol for twenty-four hours, was centrifuged and the greenish-brown liquid discarded. The extraction was carried out with 1.5-kg. portions by shaking mechanically for fifteen minutes with 1 liter methanol + 1 liter petroleum ether which formed two liquid phases. The residue was allowed to dry on trays for five–six hours and then ground in a Wiley mill No. 1 until the particles passed a 1.5 mm. sieve. The extraction was repeated three more times, as described, and all extracts were combined. The polyenes contained in the methanol layer were transferred by cautious addition of water (in 20-liter separatory funnels) into the petroleum ether (30 liters) which was then washed methanol-free. The dark red solution was dried over anhydrous calcium chloride and concentrated to 1.5 liters. When kept at 4° overnight, a greenish gummy material appeared which was removed by sucking the solution through a 4-cm. layer of calcium carbonate on a sintered glass funnel. The adsorbent was washed with a small volume of petroleum ether and the latter added to the main solution.

Isolation.—The petroleum ether solution just mentioned was developed with the same solvent on twenty-one columns[9] of Shell lime. Each column showed the following sequence after half an hour of development. (Figures on the left denote width of zones in mm.; some very narrow, pale interzones are omitted.)

2 brown
2 red
5 orange
17 red-orange, lycopene
40 pale orange, undifferentiated
17 red-orange
40 orange, prolycopene
18 yellow
6 pale interzone
36 orange, pro-γ-carotene
7 yellow
2 orange
65 orange, β-carotene
10 yellow
8 fluorescent; partly overlapping preceding zone

The development was continued until nine-tenths of the β-carotene zone had been washed into the filtrate. (This filtrate contained considerable amounts of phytofluene.[10]) Each column then showed the following sequence

3 brown	
6 orange	Section I
7 red-orange, lycopene	
40 pale orange, undifferentiated	
23 red-orange	
48 orange, prolycopene	Section II
20 very pale yellow	
42 orange, pro-γ-carotene	Section III
5 yellow	
4 pale orange	
6 almost colorless	Section IV
10 orange, β-carotene	

After elution, the corresponding Sections I, II, III, and IV of the twenty-one columns were combined.

The above Section I consisted mainly of all-*trans*-lycopene which was estimated photometrically.

Pro-γ-carotene.—The petroleum ether solution from Section III was rechromatographed on three columns. The combined main zones were eluted, washed free of alcohol and dried. The solution was then completely evaporated and the residue dissolved in a minimum amount of benzene. Pro-γ-carotene was obtained by adding absolute methanol dropwise at 20–25°, with stirring, until crystallization started, cooling in ice water and cautious addition of methanol up to three times the initial volume. After recrystallization at room temperature and washing the sample with 3 × 10 ml. of hot methanol in the centrifuge tube, 211 mg. of pure pro-γ-carotene was obtained, m. p. 134–5°. In a mixed chromatogram test there was no separation from an authentic sample.

Prolycopene.—The eluate of Section II (from 21 columns), after transfer into petroleum ether, was rechromatographed on twelve columns.

10 pale orange	
35 almost colorless	
2 yellow	
1 purple	
10 pale orange	Section V
2 yellow	
1 purple	
30 pale orange	Section VI
4 pale interzone	
8 red-orange	
1 pale interzone	
10 red-orange	Section VII
1 pale interzone	
6 red-orange	
35 orange, prolycopene	Section VIII
8 yellow	Section IX
3 orange	

Section VIII was rechromatographed on three columns. Upon development with 4% acetone in petroleum ether, the three main zones were combined and, after transfer into petroleum ether, the latter was evaporated to dryness. The residue was crystallized as given above for pro-γ-carotene; after recrystallization, 735 mg. of pure prolycopene, m. p. 111.5–112.5°, was obtained which did not separate, in a mixed chromatogram test, from an authentic sample.

Section VI was developed on three columns with petroleum ether + 4% acetone.

2 brown
8 red-orange
4 pale interzone
80 dark orange, poly-*cis*-lycopene I
100 several minor zones (added to Section VII)

The three combined 80 mm. zones were rechromatographed on a single column. The main zone of this chro-

(9) The size of the columns referred to in the following text is 30 × 8 cm. unless otherwise specified.

(10) L. Zechmeister and A. Sandoval, THIS JOURNAL, **68**, 197 (1946).

matogram was transferred into petroleum ether and evaporated. The crystallization of its residue was carried out as for pro-γ-carotene (yield, 45 mg. of poly-*cis*-lycopene I; after recrystallization, m. p. 93–95°).

The total of Sections VII (from 12 columns) was developed on twelve columns with petroleum ether + 8% acetone.

8 pale orange	
6 purple	
4 pale interzone	
10 pale orange	
6 pale interzone	
4 pale orange	
10 pale interzone	
12 dark orange	
6 pale interzone	
56 pale orange	Section X
18 red-orange	
4 yellow	
3 pale interzone	
40 red-orange	Section XI
8 pale yellow	
40 pale red	Section XII
16 pale orange	

Section X (from 12 columns) was developed with 6% acetone in petroleum ether on three columns.

15 several minor zones	
30 colorless	
80 pale orange	Section XIII
40 red-orange	Section XIV
30 several minor zones	

Section XIII (from 3 columns) was developed with 6% acetone in petroleum ether on a single column. The main zone was transferred into petroleum ether and evaporated. The residue crystallized from benzene and methanol.[11] The yield after recrystallization was 14 mg. of poly-*cis*-lycopene II, m. p. 85–87°.

Section XIV (from 3 columns) was developed on a single column with petroleum ether and 6% acetone. The main zone was treated as just described. Yield, after recrystallization from benzene–methanol, was 19 mg. of poly-*cis*-lycopene III, m. p. 105–106°.

Section XI (from 12 columns) was developed on four columns with petroleum ether and 4% acetone. The combined main zones were transferred into petroleum ether, evaporated and crystallized. After recrystallization, 42 mg. of all-*trans*-γ-carotene was obtained with the constant m. p. 128–129°. In the mixed chromatogram test it did not separate from an authentic sample.

Section XII (from 12 columns) was developed on three columns with petroleum ether and 6% acetone. The three combined main zones were transferred into petroleum ether. After a like development on a single column, the main zone was evaporated and the residue was crystallized. After recrystallization, 47 mg. of neo-γ-carotene P, m. p. 89–90°, resulted. The main pigment obtained by iodine catalysis from this isomer did not separate from γ-carotene (*ex Mimulus*) in the mixed chromatogram test.

Section IX was developed on three columns with petroleum ether and 2% acetone.

5 brown
2 colorless
18 several minor zones
100 orange, prolycopene
60 yellow (lower part orange)
8 red-orange, pro-γ-carotene
10 yellow

After transfer into petroleum ether, the three combined 60-mm. zones were developed with petroleum ether and 4% acetone on two columns.

15 several minor zones
130 bright yellow
40 yellow and pale orange zones
4 red-orange

The two combined 40-mm. zones were developed on a single column (25 × 4.5 cm.) with petroleum ether and 4% acetone.

10 several minor zones
6 colorless
60 pale yellow, poly-*cis*-lycopene IV
5 almost colorless
80 yellow, poly-*cis*-lycopene V
3 pale yellow
20 yellow-orange, poly-*cis*-lycopene VI

Each poly-*cis* compound was rechromatographed. Since the quantity of these pigments was not sufficient for the preparation of crystalline samples, in order to determine the extinction curves, the solvent was displaced from the columns with 65 ml. of optically pure hexane. After elution, the respective pigments were transferred into hexane. The concentrations were determined, upon iodine catalysis, using the value, $E^{mol.}_{1cm.} = 14.6 \times 10^4$ at 468–469 mμ which is the average of the figures obtained with four independent samples and only slightly different from some data given earlier.

Summary

Six poly-*cis*-lycopenes, $C_{40}H_{56}$, which contain most of their sterically available double bonds in *cis* configuration occur in the ripe berries of *Pyracantha angustifolia* Schneid. Three such compounds as well as prolycopene, pro-γ-carotene and a new mono-*cis* isomer of the latter were isolated in pure crystalline state. The spectral and adsorption characteristics of the new poly-*cis*-lycopenes are in accordance with some earlier data and discussions.

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(11) For the drawing in Fig. 1, poly-*cis*-lycopene II was crystallized from petroleum ether + methanol with addition of enough ethanol to prevent two liquid phases.