652. *Carotenoids and Related Compounds. Part II.** C_{10} *Intermediates for the Synthesis of Carotenoids.*

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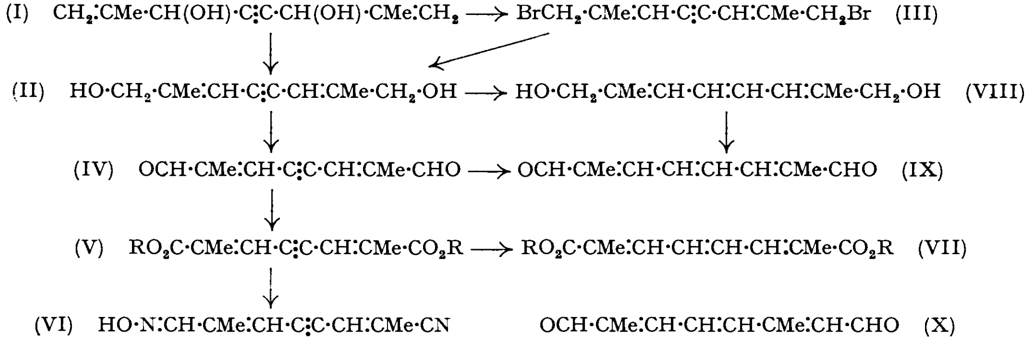
A number of C_{10} intermediates for the synthesis of carotenoids and derived compounds have been prepared.

All routes so far developed for the total synthesis of a carotenoid consist in the chain extension, in both directions simultaneously, of a small central unit. As the latter, acetylene (C_2), diacetylene (C_4), and oct-4-ene-2 : 7-dione (C_8) have each been employed (for reviews see *Ann. Reports,* 1950—1952). In connection with the programme outlined in Part I (preceding paper), the use of larger intermediates for introducing the central portion of the final molecule seemed to offer certain advantages. The preparation of suitable compounds was therefore undertaken, and in this paper convenient syntheses of a number of C_{10} intermediates are described.



$$\begin{tikzcd}
\text{(I)}\ CH_2{:}CMe{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CH(OH){\cdot}CMe{:}CH_2 \arrow[r] \arrow[d] & BrCH_2{\cdot}CMe{:}CH{\cdot}C{\vdots}C{\cdot}CH{:}CMe{\cdot}CH_2Br\ \text{(III)} \arrow[dl] \\
\text{(II)}\ HO{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}C{\vdots}C{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}OH \arrow[r] \arrow[d] & HO{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}OH\ \text{(VIII)} \arrow[d] \\
\text{(IV)}\ OCH{\cdot}CMe{:}CH{\cdot}C{\vdots}C{\cdot}CH{:}CMe{\cdot}CHO \arrow[r] \arrow[d] & OCH{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CHO\ \text{(IX)} \\
\text{(V)}\ RO_2C{\cdot}CMe{:}CH{\cdot}C{\vdots}C{\cdot}CH{:}CMe{\cdot}CO_2R \arrow[r] \arrow[d] & RO_2C{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CO_2R\ \text{(VII)} \\
\text{(VI)}\ HO{\cdot}N{:}CH{\cdot}CMe{:}CH{\cdot}C{\vdots}C{\cdot}CH{:}CMe{\cdot}CN & OCH{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CHO\ \text{(X)}
\end{tikzcd}$$

The formation in 50% yield of a crystalline glycol (I) (m. p. 71°), by the Grignard reaction of acetylene with α-methylacraldehyde, was reported by Deemer, Lutwak, and Strong (*J. Amer. Chem. Soc.*, 1948, **70**, 154). Using slightly different experimental conditions we have repeated this reaction several times and always obtained, in similar yield, a higher-melting (92°) form of the glycol; this diastereoisomeride closely resembles a product from one preparation by Deemer *et al.*

The American authors rearranged the low-melting glycol (I) to its fully conjugated isomer (II) by heating it with aqueous alcoholic sulphuric acid. Only low yields (10%) of crystalline product were however isolated, probably owing to partial etherification of the glycol during isomerisation (cf. Heilbron, Jones, and Weedon, *J.*, 1945, 81). In the present studies higher yields (up to 60%) of crystalline diprimary glycol (II) have been obtained by treating (I) with phosphorus tribromide, and hydrolysis of the resulting dibromide (III)

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* Part I, preceding paper.

via the diacetate. Attempts by Deemer *et al.* to oxidise the glycol (II) to the corresponding dialdehyde, or to reduce it to a triene glycol, were unsuccessful. By methods recently developed, both these transformations have now been effected almost quantitatively.

By oxidation of the diprimary glycol (II), in acetone with manganese dioxide (cf. Part I), the dialdehyde (IV) was prepared (95%). Chromic acid oxidation of the dialdehyde gave in 95% yield the diacid (V; R = H) which was also obtained, but only in 30% yield, by direct oxidation of the glycol (II). Esterification with diazomethane gave the dimethyl ester (V; R = Me). Attempts to prepare the corresponding dinitrile by dehydration of the dioxime of (IV) with acetic anhydride were unsuccessful, the nitrile-oxime (VI) being isolated.

Partial hydrogenation of the diester (V; R = Me) over Raney nickel, or lead-poisoned palladium (Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446), gave (90—95%) a triene diester (VII; R = Me) which, by irradiation in the presence of a trace of iodine, was converted into a higher-melting isomer. It is believed that the initial hydrogenation product has a *cis*-configuration about the central double bond, in agreement with the known stereochemical course of reduction over palladium and nickel catalysts (cf. Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 148), and that on irradiation it rearranges into the " all-*trans* "-form. Hydrolysis of the two diesters (VII; R = Me) gave different isomeric dioic acids (VII; R = H), or half esters, depending on the experimental conditions.

Partial reduction of the glycol (II) over Lindlar's catalyst gave, almost quantitatively, a triene glycol (VIII) which was oxidised, in acetone with manganese dioxide, to the triene dialdehyde (IX) in 85% yield. The same product was also obtained (80%) by reduction of the acetylenic dialdehyde (IV).

The triene glycol (VIII) is probably a *trans-cis-trans*-isomer; on irradiation (iodine) it yielded complex mixtures. Surprisingly, the triene dialdehyde (IX) was recovered after irradiation (iodine) or fusion, and it is therefore tentatively assigned the " all-*trans* "-structure, stereomutation about the central bond being assumed to have taken place spontaneously in solution at room temperature. The possibility that the dialdehyde contains a *cis*-double bond which is preserved during irradiation and fusion is considered unlikely, but cannot be definitely excluded. It is noteworthy that a higher-melting C_{10} dialdehyde, exhibiting light-absorption maxima at very similar wave-lengths to those of the synthetic dialdehyde reported above, was isolated (6—8%) by Wendler, Rosenblum, and Tishler (*J. Amer. Chem. Soc.*, 1950, **72**, 234) as a by-product in the oxidation of β-carotene with hydrogen peroxide–osmium tetroxide. From its mode of formation, this degradation product is, presumably, an " all-*trans* "-isomer, and of the two conceivable structures, (IX) and (X), Wendler *et al.* favour (IX). Whether the differences between the two dialdehydes are due to polymorphism, or to structural or geometrical isomerism, is at present uncertain.

	Acetylenic series		" Mono-*cis* " series		" All -*trans* " series	
	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
Glycol (III) or (VIII)	263 *	19,500	—	—	—	—
	271	26,000	281	39,000	—	—
	287	21,000	292	30,000	—	—
Dialdehyde (IV) or (IX) †	308	35,000	—	—	306	30,000
	327		—	—	320	47,500
					336	42,500
Diester (V or VII; R = Me)	305	30,000	316	38,000	320	51,000
	322	26,000	323 *	32,500	330	45,000
Half-ester of (V or VII; R = H)	—	—	315	37,000	314	49,000
	—	—	323 *	31,000	327	39,000
Diacid (V or VII; R = H)	305	26,000	315	44,000	315	49,000
	—	—	327	41,000	326	43,000

*Inflexion. † In *n*-hexane.

All the compounds described above exhibited the expected light-absorption properties, most of which are given in the Table (wave-lengths in mμ). The acetylenic compounds have maximal absorption at wave-lengths 10—15 mμ shorter than those of the corresponding polyenes (cf. Part I). As with the geometrical isomers of muconic acid and its derivatives (Elvidge, Linstead, Sims, and Orkin, *J.*, 1950, 2235; Elvidge, Linstead, and Sims, *J.*, 1951, 3386; 1953, 1793), the "mono-*cis*"- and "all-*trans*"-form of the acid (VII; R = H), and its di- and half-ester, have maximal absorption at almost identical wave-lengths, but of slightly different intensity.

An account of the work covered by this and the following paper was given at the Chemical Society Symposium on Acetylene Chemistry (cf. *Chem. and Ind.*, 1953, 239). Inhoffen, Isler, Bey, Raspé, Zeller, and Ahrens (*Annalen*, 1953, **580**, 7) meanwhile have reported the preparation of the acetylenic dialdehyde (IV), and its use in the synthesis of crocetin. The glycol (II) was prepared by the method of Deemer *et al.* (the yield from the isomerisation being raised to 30%), and oxidised to (IV) by a process very similar to that described here.

EXPERIMENTAL

See notes preceding Experimental section of Part I.

2 : 7-*Dimethylocta*-1 : 7-*dien*-4-*yne*-3 : 6-*diol* (I).—Benzene (1 l.) was added to a solution of ethylmagnesium bromide (from 24 g. of magnesium) in ether (500 c.c.), and the majority of the ether was then distilled off. The resulting solution was cooled and stirred vigorously. A rapid stream of acetylene (purified by passage through acidified copper sulphate solution, chromic acid, concentrated sulphuric acid, and finally over phosphoric oxide) was passed through the solution for 3 hr. To the pale grey suspension thus obtained freshly distilled α-methylacraldehyde (70 g.) was added during 45 min., and the mixture was stirred overnight, giving a clear solution. The Grignard complex was decomposed by the addition of saturated aqueous ammonium chloride, and the benzene layer was then separated, washed with water, dried (Na_2SO_4), and evaporated.

The viscous residue (72 g.) crystallised partly during a few days at 0°. The solid was freed from oil by trituration at 0° with a small amount of benzene. Crystallisation from benzene or chloroform–light petroleum (b. p. 60—80°) gave the glycol as plates (42 g., 50%), m. p. 91—92° (Found: C, 72·25; H, 8·8. Calc. for $C_{10}H_{14}O_2$: C, 72·25; H, 8·5%) (Deemer, Lutwak, and Strong, *J. Amer. Chem. Soc.*, 1948, **70**, 154, give m. p. 70·5—71·5°, but in one experiment isolated an isomeric product, m. p. 88—91°).

1 : 8-*Dibromo*-2 : 7-*dimethylocta*-2 : 6-*dien*-4-*yne* (III).—Phosphorus tribromide (78 g.) was added dropwise at 20° to a well-stirred suspension of the preceding crystalline glycol (20·0 g.) in benzene (160 c.c.), and the mixture was stirred for a further 5 hr. Ice and water were added and the mixture was extracted with ether (3 × 70 c.c.). The combined extracts were washed with sodium hydrogen carbonate solution, dried, and evaporated. The residue crystallised at 0°. Low-temperature crystallisation from light petroleum (b. p. 60—80°) gave the *dibromide* as needles (25 g., 70%), m. p. 49—50° (Found: C, 41·05; H, 4·3. $C_{10}H_{12}Br_2$ requires C, 41·1; H, 4·15%). Light absorption: Max., 293 mμ; ε = 27,500. Inflexions, 279 and 302 mμ; ε = 23,000 and 23,000. Distillation of the crude dibromide gave a product, b. p. 108—110°/10^{-3} mm., m. p. 47—49°, in only 50% yield.

2 : 7-*Dimethylocta*-2 : 6-*dien*-4-*yne*-1 : 8-*diol* (II).—A solution of the preceding dibromide (25·0 g.) and anhydrous potassium acetate (24 g.) in methanol (300 c.c.) was stirred and boiled under reflux for 3—12 hr. Most of the solvent was evaporated at 20° under reduced pressure, water was added, and the product was isolated with ether, giving an oil (19·2 g., 90%) which, in methanol (55 c.c.), was warmed at 50—55° with methanolic N-potassium hydroxide (380 c.c.) for 20 min. The solution was rapidly cooled and then concentrated under reduced pressure. Water was added and the product was isolated with ether. Crystallisation from acetone–light petroleum (b. p. 60—80°) gave the glycol (12·0 g.) as needles, m. p. 113° (Found: C, 71·95; H, 8·35. Calc. for $C_{10}H_{14}O_2$: C, 72·25; H, 8·5%). Light absorption: see Table. [*Idem, loc. cit.*, give m. p. 109—110° and light absorption: max., 270, 286, and 333 mμ (ε = 27,000, 21,000, and 1400 respectively).]

The yield in the hydrolysis was variable (50—90%). In some experiments the crude diacetate was distilled, giving an oil, b. p. 120°(bath-temp.)/10^{-4} mm., n_D^{25} 1·5170.

Bromination of the crude viscous product obtained from the Grignard reaction after removal of the crystalline glycol (I), and subsequent hydrolysis of the resulting dibromide, gave the rearranged glycol, m. p. 113°, in *ca.* 10% overall yield.

2 : 7-*Dimethylocta*-2 : 6-*dien*-4-*ynedial* (IV).—The preceding glycol (3·0 g.) in acetone (300 c.c.) was shaken with manganese dioxide (60 g.) at 20° for 24 hr. Removal of oxide and solvent, and crystallisation of the residue (2·9 g.), m. p. 67—68°, from aqueous methanol gave the dialdehyde as needles, m. p. 69·5—70° (Found: C, 74·15; H, 6·4. Calc. for $C_{10}H_{10}O_2$: C,

75·05; H, 6·2%) (Inhoffen, Isler, Bey, Raspé, Zeller, and Ahrens, *Annalen*, 1953, **580**, 7, give m. p. 68°). Light absorption : see Table. The *dioxime*, prepared in 85% yield, crystallised from aqueous pyridine in needles, m. p. 234·5° (Found : N, 14·6. $C_{10}H_{12}O_2N_2$ requires N, 14·55%). Light absorption : Max., 324 and 343 mμ; ε = 42,500 and 38,500 respectively.

7-*Cyano-2-methylocta-2 : 6-dien-4-ynaldoxime* (VI).—A solution of the preceding dialdoxime (220 mg.) in acetic anhydride (66 c.c.) was heated under reflux for 15 min. and then evaporated. Chromatography of the residue in benzene on alumina (*ca.* 50 g.; grade IV), and elution of the main pale yellow band with benzene–methanol (95 : 5), yielded a solid (170 mg.), m. p. 148°. Crystallisation from aqueous methanol gave the *nitrile-oxime* as needles, m. p. 152° (Found: C, 68·75; H, 6·0. $C_{10}H_{10}ON_2$ requires C, 68·9; H, 5·8%). Light absorption : Max., 319 and 328 mμ; ε = 31,500 and 31,500.

2 : 7-*Dimethylocta-2 : 6-dien-4-ynedioic Acid* (V; R = H).—(a) *From 2 : 7-dimethylocta-2 : 6-dien-4-ynedial.* A solution of chromium trioxide (1·4 g.) and concentrated sulphuric acid (2·24 g.) in water (7 c.c.) was added to a stirred and cooled (ice-bath) solution of 2 : 7-dimethylocta-2 : 6-dien-4-ynedial (1·37 g.) in acetone (40 c.c.) at such a rate as to keep the temperature at 10°. The mixture was stirred for 2 hr. at 20°, diluted with water, and then thoroughly extracted with ether. The acidic material was isolated by extraction of the ethereal solution with saturated aqueous sodium hydrogen carbonate in the usual way, giving a pale yellow powder (1·55 g., 95%), m. p. 287°. Recrystallisation from aqueous methanol gave the *diacid* as a colourless microcrystalline powder, m. p. 302° (Found : C, 61·6; H, 5·7. $C_{10}H_{10}O_4$ requires C, 61·85; H, 5·2%). Light absorption : see Table.

All attempts to obtain the acid by oxidation of the dialdehyde with freshly prepared silver oxide (cf. Wendler, Slates, Trenner, and Tishler, *J. Amer. Chem. Soc.*, 1951, **73**, 719) failed.

(b) *From 2 : 7-dimethylocta-2 : 6-dien-4-yne-1 : 8-diol.* A solution (16 c.c.) of chromium trioxide (3·2 g.) and concentrated sulphuric acid (5·12 g.) in water was added to a stirred and cooled solution of 2 : 7-dimethylocta-2 : 6-dien-4-yne-1 : 8-diol (1·0 g.) in acetone (20 c.c.) during 30 min., the temperature being kept below 15°. The mixture was stirred at 20° for 2 hr., diluted with water, and then thorougly extracted with ether. The acidic product was isolated ($NaHCO_3$) and gave the crude diacid (0·35 g., 30%) as a pale yellowish powder, m. p. 278°. Recrystallisation from aqueous methanol, or from acetone–light petroleum (b. p. 60—80°) gave the diacid as a colourless microcrystalline powder, m. p. and mixed m. p. with a specimen from (a), 302°.

Methyl 2 : 7-Dimethylocta-2 : 6-dien-4-ynedioate (V; R = Me).—To a suspension of the preceding acid (1·55 g.) in dry ether (15 c.c.) ethereal diazomethane was added at 20° in small portions, until no more nitrogen was evolved and a homogeneous solution obtained. The solution was filtered and evaporated. The residue crystallised from chloroform–light petroleum (b. p. 60—80°), or from methanol, giving the *diester* as needles (1·38 g., 78%), m. p. 113—114° (Found : C, 64·9; H, 6·45. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%). Light absorption : see Table.

Hydrolysis of the ester (100 mg.) with potassium hydroxide (1·60 g.) in methanol (50 c.c.) for 48 hr. at 20°, and isolation of the product in the usual manner, furnished the original acid (85 mg., 98%), m. p. and mixed m. p. 302°.

*Methyl 2 : 7-Dimethylocta-*trans-2 : cis-4 : trans-6-*trienedioate* (V; R = Me).—(*a*) The preceding diester (130 mg.) in ethyl acetate (10 c.c.) was shaken with Lindlar's catalyst (25 mg.; no quinoline) in hydrogen until 15·25 c.c. at 23°/758 mm. (equiv. to 1·07 double bonds) had been absorbed (rate of absorption *ca.* 4 c.c./min.). The reaction was then interrupted, the catalyst and solvent were removed, and the residue was crystallised from methanol, giving the "*mono*-cis"-*diester* (126 mg.) as needles, m. p. 98° (Found : C, 64·7; H, 6·9. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·2%). Light absorption : see Table.

When the hydrogenation was carried out in the presence of quinoline (4%), the rate of absorption was much slower (0·4—0·8 c.c./min.), and a sharp drop in rate was observed when 1 mol. of hydrogen had been taken up. The yield of product was the same (95%).

(*b*) The acetylenic diester (100 mg.) in methanol (30 c.c.) was shaken with Raney nickel (0·3 g.) in hydrogen until 1·2 mols. had been absorbed (3 c.c./min.). The reaction was then interrupted and the product isolated, giving the "mono-*cis*"-diester (90 mg.), m. p. 98°, undepressed on admixture with a sample from (*a*).

Repetition of this experiment in the presence of piperidine (2 c.c.) and zinc acetate dihydrate (0·1 g.) (cf. Oroshnik, Karmas, and Mebane, *J. Amer. Chem. Soc.*, 1952, **74**, 295) gave the same yield (90%) of product (the rate of absorption was 1 c.c./min., but fell to 0·4 c.c./min. near the end of the reaction).

*Methyl "all-*trans*"-2 : 7-Dimethylocta-2 : 4 : 6-trienedioate* (V; R = Me).—A solution of the preceding mono-*cis*-triene diester [177 mg.; from (*a*)], and a trace of iodine, in light petroleum (b. p. 60—80°) (20 c.c.) was irradiated with ultra-violet light for 4 hr. at 20°. The petroleum solution was washed with N-sodium thiosulphate and water, dried, and evaporated. The residue was crystallised from methanol giving the "*all-*trans*"-diester* as needles (150 mg.), m. p. 140—141° (Found: C, 64·55; H, 7·45%). Light absorption: see Table.

*Methyl Hydrogen 2 : 7-Dimethylocta-*trans-2 : cis-4 : trans-6-*trienedioate*.—Hydrolysis of the "mono-*cis*"-triene diester (38 mg.) with potassium hydroxide (0·64 g.) in methanol (20 c.c.) for 48 hr. at 20° gave the *half-ester* which crystallised from aqueous methanol as needles (30 mg.), m. p. 256° (Found: C, 62·35; H, 6·9. $C_{11}H_{14}O_4$ requires C, 62·8; H, 6·7%). Light absorption: see Table.

*Methyl Hydrogen "all-*trans*"-2 : 7-Dimethylocta-2 : 4 : 6-trienedioate*.—Hydrolysis of the "all-*trans*"-triene diester (17 mg.) with potassium hydroxide (0·64 g.) in methanol (20 c.c.) for 48 hr. at 20° gave the *half-ester* which separated from aqueous methanol as a microcrystalline powder (12 mg.), m. p. 292° (Found: C, 62·75; H, 7·15%). Light absorption: see Table.

2 : 7-*Dimethylocta-*trans-2 : cis-4 : trans-6-*trienedioic Acid* (VII; R = H).—Hydrolysis of the "mono-*cis*"-triene diester (53 mg.) with methanolic N-potassium hydroxide (35 c.c.) for 96 hr. at 20° gave the *diacid* which separated from aqueous methanol as crystals (37 mg.), m. p. 266° (Found: C, 61·4; H, 6·15. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·15%). Light absorption: see Table.

"*all-*trans-"-2 : 7-*Dimethylocta-2 : 4 : 6-trienedioic Acid* (VII; R = H).—Hydrolysis of the "all-*trans*"-diester (69 mg.) with methanolic N-potassium hydroxide (50 c.c.) for 6 days at 20° gave the *diacid* which separated from aqueous methanol as crystals (50 mg.), m. p. 315° (Found: C, 61·3; H, 6·5%). Light absorption: see Table.

2 : 7-*Dimethylocta-2 : 4 : 6-triene-1 : 8-diol* (VIII).—A solution of 2 : 7-dimethylocta-2 : 6-dien-4-yne-1 : 8-diol (1·0 g.) in ethyl acetate (50 c.c.) containing quinoline (1 drop) was shaken in hydrogen with Lindlar's catalyst (0·1 g.). When 1 mol. of hydrogen had been taken up (150 c.c. at 21°/767 mm.) the rate of absorption fell markedly, and the reaction was interrupted. Isolation of the product and crystallisation from acetone gave the *glycol*, in almost quantitative yield, as needles, m. p. 137° (Found: C, 71·65; H, 9·85. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). Light absorption: see Table.

Irradiation of the glycol in ethyl acetate, containing a trace of iodine, with ultra-violet light for 4 hr. gave a mixture.

2 : 7-*Dimethylocta-2 : 4 : 6-triene-1 : 8-dial* (IX) (with RASHID AHMAD).—(*a*) The preceding glycol (2·0 g.) in acetone (200 c.c.) was shaken with manganese dioxide (40 g.) at 20° for 24 hr. Removal of oxide and solvent, and crystallisation of the residue from benzene or aqueous methanol, gave the *dialdehyde* as yellow prisms (1·8 g.), m. p. 151—151·5° (Found: C, 73·2; H, 7·55. $C_{10}H_{12}O_2$ requires C, 73·15; H, 7·35%). Light absorption: see Table.

(*b*) A solution of 2 : 7-dimethylocta-2 : 6-dien-4-ynedial (1·0 g.) in ethyl acetate (50 c.c.) was shaken in hydrogen with Lindlar's catalyst (0·7 g.). After 1 mol. of hydrogen (150 c.c. at 20°/755 mm.) had been absorbed, the reaction was interrupted. Removal of catalyst and solvent, and crystallisation of the residue (0·95 g.), m. p. 137—140°, twice from benzene gave the triene dialdehyde (0·8 g.), m. p. 151°, undepressed on admixture with a specimen from (*a*).

The dialdehyde was recovered after irradiation with ultra-violet light (in the presence of a trace of iodine) for 4 hr. in ethyl acetate or chloroform, or for 24 hr. in ether; also after fusion for 3 min. followed by crystallisation of the product from benzene.

By oxidation of β-carotene with hydrogen peroxide–osmium tetroxide, Wendler, Rosenblum, and Tishler (*J. Amer. Chem. Soc.*, 1950, **72**, 234) obtained a C_{10} triene dialdehyde which crystallised from benzene–light petroleum in light orange needles, m. p. 168°. Light absorption in *iso*octane: Max., 306, 320, and 336 mμ; ε = 38,000, 59,500, and 54,000. [The authors are indebted to Dr. N. L. Wendler (personal communication) for the ε values; figures given in the Experimental section of their paper quoted are incorrect.]

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