3-4), and thoroughly extracted with chloroform. The combined extracts were washed three times with water and dried over anhydrous sodium sulfate. After the chloroform was evaporated, the residue was a brown liquid which did not yield crystalline β-keto sulfoxide. The infrared spectrum contained strong bands at 1710 and 1040 cm^{-1}.

The residue was dissolved in 10% aqueous tetrahydrofuran (450 ml). Aluminum amalgam (19.6 g of aluminum) was then freshly prepared as follows. Aluminum foil was cut into approximately 1-cm^2 pieces and immersed, all at once, in a 2% aqueous solution of mercuric chloride for 15 sec. The pieces were rinsed with absolute alcohol, then with ether, and directly put into the reaction vessel. The reaction mixture was heated at 65° for 2.5 hr after addition of the amalgam. The reaction mixture was then filtered and the filtered solid was washed with tetrahydrofuran. The filtrate was concentrated to remove most of the tetrahydrofuran, ether was added, and the ether phase was separated from the water, dried over anhydrous sodium sulfate, and evaporated. The residue was distilled, giving 4.0 g of clear liquid, bp 163-164°, 69% yield, $n^{20}{}_{D}$ 1.4151. The infrared spectrum showed a strong band at 1720 cm^{-1}. The semicarbazone had mp 152-152.2°.

Anal. Calcd for $C_9H_{19}N_3O$: C, 58.34; H, 10.34; N, 22.68. Found: C, 58.55; H, 10.35; N, 22.68.

2,6,10,14-Tetramethyl-1-pentadecene (**7**).—Compound **7** was prepared according to the procedure of Burrell and co-workers.[14] When **6c** (17.7 g, 0.066 mole) was treated with methylenetriphenylphosphorane prepared from triphenylmethylphosphonium bromide[15] (21.4 g, 0.06 mole) in an ethereal solution of phenyllithium[16] (180 ml, 0.06 mole), 13.2 g (83% yield) of **7** was obtained, bp 113° (0.5 mm), $n^{20}{}_{D}$ 1.4487. The infrared spectrum of the product contained bands at 1650 and 890 cm^{-1}.

Anal. Calcd for $C_{19}H_{38}$: C, 85.63; H, 14.37. Found: C, 85.83; H, 14.18.

Phytyl Acetate (**8**).—Paraformaldehyde (2.7 g), glacial acetic acid (7.8 g), acetic anhydride (6.6 g), and concentrated sulfuric acid (1 ml) were placed in a flask. The mixture was heated (80-90°) until the paraformaldehyde depolymerized. The solution was allowed to cool to room temperature and 8.0 g (0.03 mole) of freshly distilled **7** was added dropwise. After completion of addition, the mixture was stirred for 1.5 hr at room temperature. Three hundred cubic centimeters of water was then added to the mixture and the solution was extracted with ether. The ether was washed with water and saturated sodium bicarbonate solution until it became neutral and was then washed with water again. The ether extract was dried over magnesium sulfate and evaporated. The residue was distilled, giving 7.7 g of liquid, bp 140-165° (0.6 mm). The crude product was examined by gas chromatography, which showed four peaks. One peak coincided with that of authentic phytyl acetate and product yield was 28% (indicated by gas chromatography).

Ethyl Phytenoate (**9**).—Triethyl phosphonoacetate (11.2 g, 0.05 mole) was added dropwise at room temperature to a slurry of sodium hydride (50% in mineral oil, 2.4 g, 0.05 mole) in 100 ml of dry tetrahydrofuran. After the addition, the reaction mixture was stirred for 3 hr at room temperature until gas evolution had ceased. To the solution was added phytone (13.4 g, 0.05 mole) dropwise with stirring, then the solution was heated and refluxed with stirring for 4 hr. After cooling a large excess of water was added and the aqueous solution was extracted with ether. The residue, obtained after drying over magnesium sulfate and evaporating, was distilled giving 12.4 g (73%) of liquid, bp 143-145° (0.3 mm), $n^{20}{}_{D}$ 1.4590 (lit.[17] $n^{20}{}_{D}$ 1.4588). The product showed the expected infrared spectrum with strong bands at 1710 and 1640 cm^{-1}.

Anal. Calcd for $C_{22}H_{42}O_2$: C, 78.04; H, 12.50. Found: C, 78.01; H, 12.51.

Phytol (**10**).—Ethyl phytenoate (10.2 g, 0.03 mole) was reduced with lithium aluminium hydride (1.2 g, 0.025 mole) in dry ether (100 ml) according to the procedure of Burrell and coworkers[14] to yield 7.4 g (83% yield) of phytol, bp 153° (0.6 mm), $n^{20}{}_{D}$ 1.4633 (lit.[18] $n^{25}{}_{D}$ 1.4595). The infrared spectrum of the product contained strong bands at 3300 and 1670 cm^{-1}.

Anal. Calcd for $C_{20}H_{40}O$: C, 81.00; H, 13.60. Found: C, 81.11; H, 13.62.

Acknowledgment.—The authors wish to express their gratitude to Mr. S. Moriya and Mr. Y. Sakuma for their help in carrying out the study presented in this report. The authors are also indebted to Professor S. Abe for his kind advice.

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A Total Synthesis of Astaxanthin Dimethyl Ether

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4-Methoxy-β-ionone, which was prepared in good yield from 3-dehydro-β-ionone, served as the intermediate for a total synthesis of astaxanthin dimethyl ether (XV).

Kuhn and Sörensen[1] isolated a new pigment named astaxanthin from the eggs of lobster. They established the constitution of astaxanthin and its close relationship to astacin. In 1960, Davis and Weedon[2] reported a synthesis of astacin by an oxidation of canthaxanthin. Astaxanthin dimethyl ether (XV) has now been prepared by a total synthesis.

Henbest[3] reported the preparation of 3-substituted β-ionones III and IV from 3-bromo-β-ionone (II). The 4-substituted β-ionones which would find application for the synthesis of substituted carotenoids are not available by known methods of synthesis. We have now found that 4-methoxy-β-ionone (VI) can be prepared in good yield by addition of methyl alcohol to 3-dehydro-β-ionone (V) and used it as the basis for the synthesis of astaxanthin dimethyl ether (see Chart I).

3-Dehydro-β-ionone (V) was prepared by a modification of the procedure of Henbest.[3] β-Ionone (I) was brominated with N-bromosuccinimide in the presence of calcium oxide and sodium bicarbonate in carbon tetrachloride. Dehydrobromination with dimethylaniline and pyridine resulted in a 55% yield of V. When V was stirred in a solution of methyl alcohol and sulfuric acid at 5° for 24 hr, VI was obtained in 50% yield of fractionated product.

The methoxy C_{19}-aldehyde (IX) was prepared from 4-methoxy-β-ionone by the same sequence of reactions already described[4,5] (see Chart II).

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[1] R. Kuhn and N. A. Sörensen, *Z. Angew. Chem.*, **51**, 465 (1938).

[2] J. B. Davis and B. C. L. Weedon, *Proc. Chem. Soc.*, 182 (1960).

[3] H. B. Henbest, *J. Chem. Soc.*, 1074 (1951).

[4] O. Isler, W. Huber, A. Ronco, and M. Kofler, *Helv. Chim. Acta*, **30**, 1911 (1947).

[5] J. D. Surmatis, J. Maricq, and A. Ofner, *J. Org. Chem.*, **23**, 157 (1958).

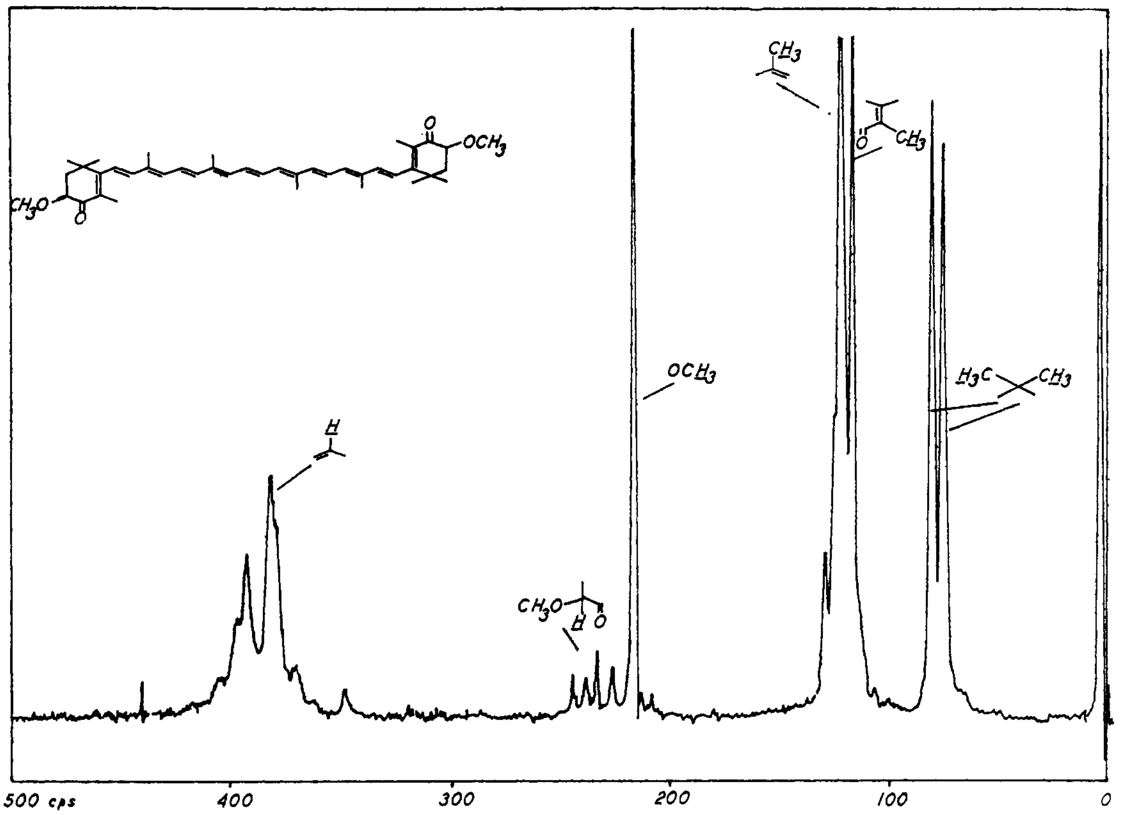


Figure 1.

Chart I

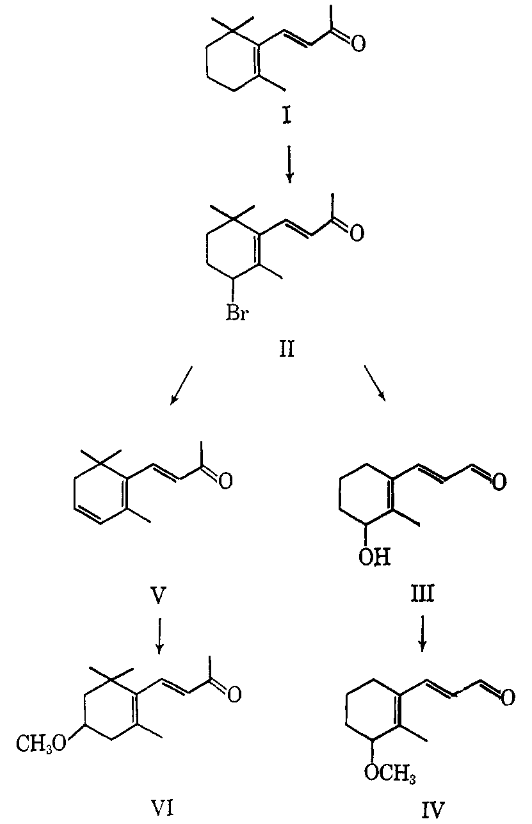
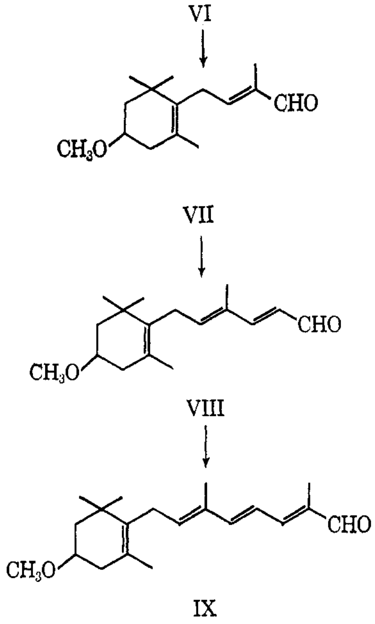


Chart II



To prepare the acetylenic diol (X), 2 moles of IX was condensed with ethynebismagnesium bromide. Dehydration and rearrangement of X was effected with hydrogen chloride in methyl alcohol to yield 15,15′-dehydro zeaxanthin dimethyl ether (XI) in 65% yield as an orange, crystalline solid, mp 147°. The structure assigned to XI was verified by its conversion to *trans*-zeaxanthin dimethyl ether. Selective reduction[6] of XI, followed by heating at 90–95° for 24 hr resulted in the formation of *trans*-zeaxanthin dimethyl ether (XII, 70%) as red needles, mp 176°. The synthetic sample could not be distinguished, by mixture melting point or infrared spectra measured in KBr, from zeaxanthin dimethyl ether prepared from an authentic sample of zeaxanthin by the procedure of Karrer and Takahashi.[7] The absorption spectra of a sample of XII measured

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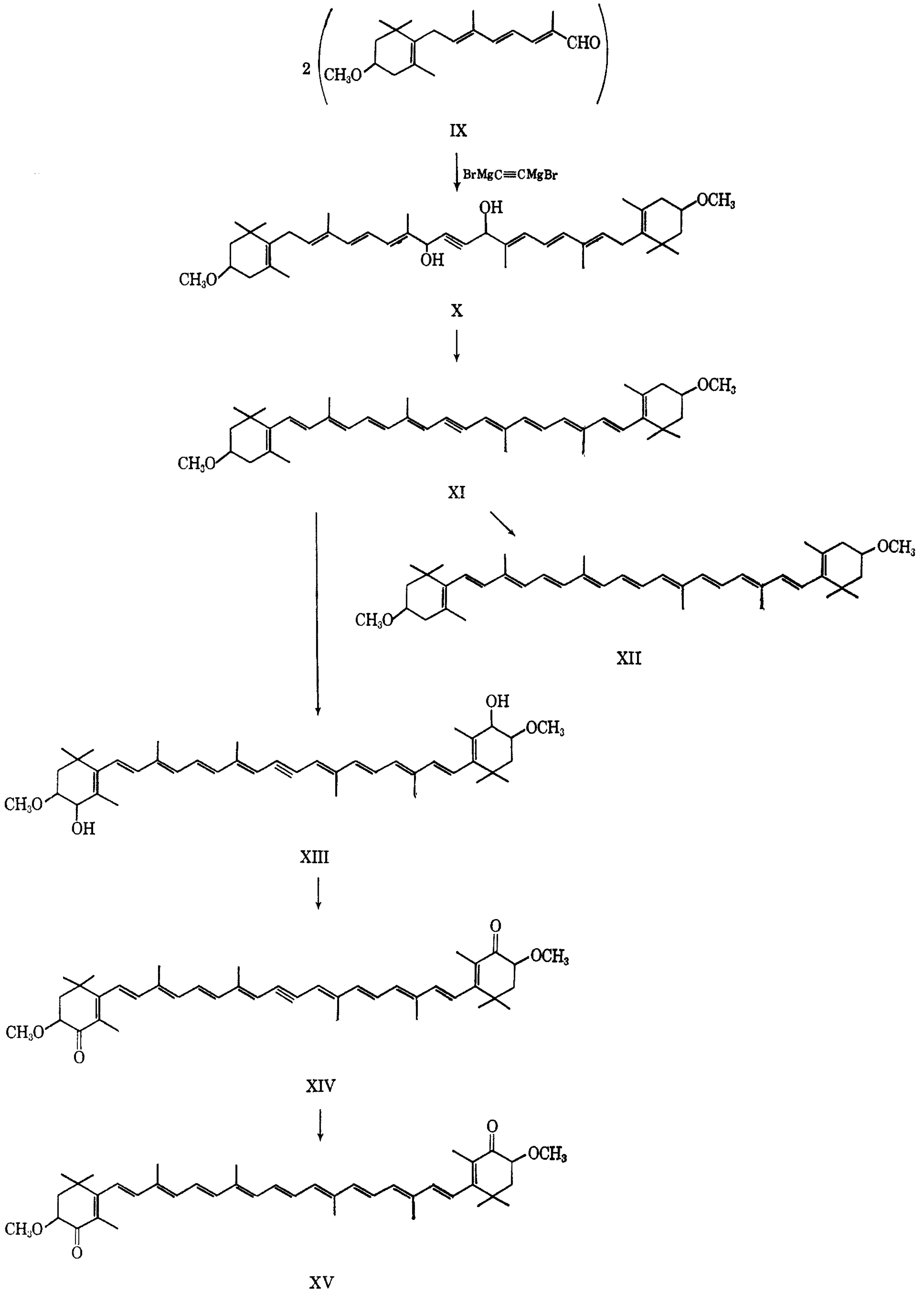
(6) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(7) P. Karrer and T. Takahashi, *ibid.*, **16**, 1163 (1933).

CHART III



in visible light agreed completely with that of the authentic sample with maxima at 452 and 480 mμ (in cyclohexane).

Dehydro zeaxanthin dimethyl ether (XI) was treated with N-bromosuccinimide in chloroform and acetic acid. Reaction with diethylaniline followed by saponification with potassium hydroxide afforded XIII as an orange, crystalline solid. Oxidation of XIII with aluminium isopropoxide gave XIV as a red, crystalline solid, mp 202°. Selective reduction of XIV afforded astaxanthin dimethyl ether, which crystallized as red needles from methylene chloride–methyl alcohol, mp 212° (see Chart III). The nuclear magnetic resonance (nmr) spectrum[8] showed 14 olefinic protons at δ 6.0–6.9; two (>CHO) protons at δ 3.92; two (OCH_3) groups at δ 3.60; six ($CH_3C{=}$) groups at δ 1.8–2.2; and two *gem*-dimethyl groups at δ 1.23 and 1.27 (see Figure 1).

Experimental Section[9]

4-(2,6,6-Trimethyl-1,3-cyclohexadien-1-yl-3-buten-2-one (V).—β-Ionone (366 g) in carbon tetrachloride (2.5 l.) was placed in a 5-l., round-bottom flask fitted with an efficient coil condenser, mechanical stirrer, and a thermometer. Sodium bicarbonate (200 g), calcium oxide (160 g), and N-bromosuccinimide (428 g) were added, the mixture was heated until boiling began, and the external heat was removed while vigorous boiling continued for about 10 min. When the exothermic reaction subsided, the temperature was lowered to 40°, dimethyl aniline (550 ml) was added, and the succinimide was filtered through a fritted-glass funnel and washed with carbon tetrachloride. The solvent was distilled until the pot temperature reached 90°, and the residue was heated under an atmosphere of nitrogen for 2 hr with a water bath. Pyridine (180 ml) was added, and heating was continued for 1 hr longer. The cooled reaction mixture was poured onto cold water and extracted with petroleum ether (bp 30–60°). The combined extracts were washed with cold 2% sulfuric acid, water, and sodium bicarbonate solution. Vacuum distillation yielded 199 g (55%) of V, bp 80–86° (0.2 mm), $n^{25}\text{D}$ 1.555. *Anal.* Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.53. Found: C, 81.80; H, 9.45.

4-(2,6,6-Trimethyl-4-methoxy-1-cyclohexen-1-yl)-3-buten-2-one (VI).—Concentrated sulfuric acid (72 ml) in methyl alcohol (1.8 l.) was cooled to 2° in a 5-l. flask fitted with a stirrer and a thermometer. Dehydro-β-ionone (V, 180 g) was added to the cold solution and stirred under an atmosphere of nitrogen at 2–5° for 24 hr. The reaction mixture was poured onto ice water (1.8 l.) in a glass separatory funnel provided with an air stirrer, and a 50% aqueous solution of sodium hydroxide (250 ml) was stirred into the cold reaction mixture. After stirring for several minutes, the product was extracted with petroleum ether, and the combined extracts were washed with water and dried over Drierite. Vacuum distillation yielded 104 g (50%) of VI, bp 80–86° (0.08 mm), $n^{25}\text{D}$ 1.5160, $E^{1\%}_{1\,\text{cm}}$ (291 mμ) 398 (ethyl alcohol). *Anal.* Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98. Found: C, 75.60; H, 9.75.

4-(2,6,6-Trimethyl-4-methoxy-1-cyclohexen-1-yl)-2-methyl-2-buten-1-al (VII).—To a 3-l., three-neck flask equipped with an efficient stirrer, thermometer, and a nitrogen inlet tube were charged 4-(2,6,6-trimethyl-4-methoxy-1-cyclohexen-1-yl)-3-buten-2-one (VI, 98.5 g), ethyl chloroacetate (145 g), and methyl alcohol (46 ml). The solution was cooled to −20° and sodium methoxide (81 g) was added in small portions during 2 hr. The reaction temperature was maintained at −5 to −10° during the addition, and stirring was continued for 2 hr longer at 0°. A solution of sodium hydroxide (60 g) in methyl alcohol (420 ml) was stirred into the reaction mixture. Cold water (1.2 l.) was added, and the stirring was continued under an atmosphere of nitrogen for 1 hr. The product was extracted with petroleum ether, washed until neutral, and isolated by distillation to give 67.8 g (70%) of VII, bp 95–98° (0.1 mm), $n^{25}\text{D}$ 1.507, $E^{1\%}_{1\,\text{cm}}$ (230 mμ) 760 (ethyl alcohol). *Anal.* Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24; methoxyl, 13.13. Found: C, 76.41; H, 10.28; methoxyl, 13.05.

6-(2,6,6-Trimethyl-4-methoxy-1-cyclohexen-1-yl)-4-methyl-2,4-hexadien-1-al (VIII).—Compound VII (200 g) was converted to the acetal by stirring with triethylorthoformate (160 ml) and 85% phosphoric acid (2 ml) for 24 hr at 20–25°, under an atmosphere of nitrogen. The reaction mixture was cooled to −10°, and a 10% solution of zinc chloride in ethyl acetate (20 ml) was added. Freshly distilled ethyl vinyl ether (152 ml) was added dropwise at −10° over 2 hr. The cold bath was removed, and stirring was continued overnight.

A solution of sodium acetate (84 g) in acetic acid (720 ml) and water (72 ml) was added to the reaction flask which was then heated at 95° for 2 hr with a hot water bath. The cooled solution was diluted with water (2 l.) and extracted with benzene. Vacuum distillation of the solvent and crystallization of the residue from petroleum ether (bp 60–80°) yielded 133 g (60%) of VIII as a pale yellow, crystalline solid, mp 72°, $E^{1\%}_{\text{cm}}$ (281 mμ) 1200 (ethyl alcohol). *Anal.* Calcd for $C_{17}H_{26}O_2$: C, 77.87; H, 9.98; methoxyl, 11.82. Found: C, 77.58; H, 9.70; methoxyl, 11.87.

8-(2,6,6-Trimethyl-4-methoxy-1-cyclohexen-1-yl)-2,6-dimethyl-2,4,6-octatrien-1-al (IX).—Compound IX was prepared by a procedure similar to that described for VIII except that ethyl propenyl ether was condensed with the acetal of VIII. It was obtained in 79.2% yield as a yellow, crystalline solid, mp 42°, $E^{1\%}_{1\,\text{cm}}$ (325 mμ) 1599 (ethyl alcohol). *Anal.* Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 9.99; methoxyl, 10.25. Found: C, 79.16; H, 9.67; methoxyl, 10.15.

1,18-Bis(2,6,6-trimethyl-4-methoxy-1-cyclohexen-1-yl)-3,7,12,16-tetramethyloctadecahexen-2,4,6,12,14,16-yne-9-diol-8,11 (X).—Ethynebismagnesium bromide was prepared by bubbling dry acetylene for 24 hr into ethylmagnesium bromide obtained from magnesium turnings (31.8 g), ethyl bromide (162 g), and dry ethyl ether (620 ml). A solution of IX (120 g) in ether (500 ml) was added rapidly to the stirred reaction mixture, which was then refluxed for 2 hr. The resulting Grignard complex was poured onto crushed ice, and cold, dilute sulfuric acid (5%) was added until the mixture was faintly acid. The ether solution containing the product was washed until neutral with sodium bicarbonate and then with water and dried over Drierite. Removal of the solvent *in vacuo* afforded X as a pale yellow, waxy solid which was pure enough for use in the next step.

1,18-Bis(2,6,6-trimethyl-4-methoxy-1-cyclohexen-1-yl)-3,7,12,16-tetramethyloctadecaocten-1,3,5,7,11,13,15,17-yne-9 (15,15′-Dehydro Zeaxanthin Dimethyl Ether, XI).—To a solution of the crude diol (X) in ethyl ether (1.2 l.) and methyl alcohol (300 ml) was added a solution (300 ml) of 6 *N* hydrogen chloride in methanol. After stirring for 10 min, crystals of the acetylenic carotenoid (XI) appeared. This was stored overnight at 0°. The product was filtered in an inert atmosphere and washed successively with sodium bicarbonate solution, water, and methyl alcohol. After recrystallization from benzene, there was obtained 77.4 g (65%) of XI, mp 147°. *Anal.* Calcd for $C_{42}H_{58}O_2$: C, 84.79; H, 9.81; methoxyl, 10.43. Found: C, 84.68; H, 9.52; methoxyl, 10.46.

Zeaxanthin Dimethyl Ether XII.—A suspension of XI (27 g) in heptane (300 ml) was hydrogenated in the presence of Lindlar's catalyst[6] until 1 molar equiv of hydrogen was consumed. The suspension was heated to boiling before filtration of the catalyst, which was washed thoroughly with additional portions of hot solvent. Finally, the filtrate was concentrated until a pasty mass remained. This was heated at 90° for 16 hr under an atmosphere of nitrogen to effect transformation to the *trans* compound.[5] Filtration and recrystallization from benzene afforded 19 g (70%) of *trans*-zeaxanthin dimethyl ether (XII), mp 176°, absorption maxima at 452 and 480 mμ (cyclohexane), $E^{1\%}_{1\,\text{cm}}$ (452 mμ) 2200. *Anal.* Calcd for $C_{42}H_{60}O_2$: C, 84.51; H, 10.13; methoxyl, 10.39. Found: C, 84.18; H, 9.93; methoxyl, 10.58.

1,8-Bis(3-hydroxy-4-methoxy-2,6,6-trimethyl-1-cyclohexen-1-yl)-3,7,12,16-tetramethyl-1,3,5,7,11,13,15,17-octadecaoctaen-9-yne (XIII).—A solution of XI (5 g) in alcohol-free chloroform (500 ml) was placed in a flask fitted with an efficient stirrer and cooled to −18°. A solution of N-bromosuccinimide (3.3 g) in alcohol-free chloroform (800 ml) and glacial acetic acid (15 ml) was added all at once, and the reaction was stirred vigorously for 30 sec. Diethyl aniline (40 ml) was added, stirring was continued for 2 hr under an atmosphere of nitrogen with the cold bath removed, and the reaction mixture was washed with cold, dilute (5%) sulfuric acid, water, sodium bicarbonate, and finally with water. The solvent was distilled under vacuum and the residue was dissolved in benzene (50 ml). A solution of potassium hydroxide (5 g) in methyl alcohol (100 ml) was added and the solution was refluxed for 2 hr. Most of the solvent was distilled under vacuum, and the resulting syrup was crystallized from benzene–petroleum ether (bp 60–80°). Recrystallization from benzene afforded 1.8 g (30%) of XIII as an orange, crystalline solid. An analytical sample after three recrystallizations from benzene melted at 194°. The absorption spectrum had

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[8] The nuclear magnetic resonance (nmr) spectrum was obtained with a Varian A-60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as the internal reference (δ = 0 ppm).

[9] The boiling and melting points are uncorrected. The melting points were determined in vacuum capillaries.

maxima at 432 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 1490) and 457 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 1213) (cyclohexane). *Anal.* Calcd for $C_{42}H_{58}O_4$: C, 79.45; H, 9.21; methoxyl, 9.77. Found: C, 79.46; H, 9.30; methoxyl, 9.81.

1,18-Bis(4-methoxy-2,6,6-trimethyl-1-cyclohexen-3-on-1-yl)-3,7,12,16-tetramethyl-1,3,5,7,11,13,15,17-octadecaoctaen-9-yne (XIV).—A solution of XIII (3.8 g) in toluene (200 ml) was added to a reaction flask containing cyclohexanone (100 ml) and aluminum isopropoxide (10 g), and the mixture was stirred at reflux under an atmosphere of nitrogen until tlc indicated that the oxidation was complete. The mixture was poured onto cold, dilute (5%) sulfuric acid and washed until neutral, and the solvent was distilled under vacuum. After recrystallization from benzene, XIV was obtained as a red, crystalline solid, 3.3 g (87%), mp 202°. *Anal.* Calcd for $C_{42}H_{54}O_4$: C, 80.97; H, 8.74. Found: C, 81.04; H, 9.01.

1,18-Bis(4-methoxy-2,6,6-trimethyl-1-cyclohexen-3-on-1-yl)-3,7,12,16-tetramethyl-1,3,5,7,9,11,13,15,17-octadecanonene (XV).—A suspension of XIV (2 g) in heptane (150 ml) was hydrogenated with Lindlar's catalyst by the procedure already described for the preparation of XIV. Recrystallization from methylene chloride–methyl alcohol afforded 1.5 g (75% of XV as red needles, mp 212°. The absorption spectrum had maxima at 467 (in cyclohexane) and 485 mμ (in pyridine). *Anal.* Calcd for $C_{42}H_{56}O_4$: C, 80.71; H, 9.04; methoxyl, 9.92. Found: C, 80.93; H, 9.21; methoxyl, 10.27.

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Transformations of Fusidic Acid. III.
17-Oxa-4α,8,14-trimethyl-D-homo-18-norandrostanes[1,2]

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A new and unexpected series of compounds (**4**) containing a ring-D lactol acetate has been obtained from the ozonolysis of fusidic acid derivatives. Sodium borohydride reduction deacetoxylated these compounds and gave the ring D lactones (**8** and **9**). The epimerization of the 9β-11-keto lactones to the 9α derivatives has been carried out and the stereochemistry of the epimers demonstrated by molecular-rotation differences and ORD measurements. Differences of chemical reactivity in the 9α and 9β series have been observed. Nmr and infrared spectral data for these compounds have been presented.

The presence of a 17,20 double bond in fusidic acid[3] (**1a**) presents a convenient handle for the elimination of the side chain by ozonolytic techniques. This is the method which was used by Godtfredsen and coworkers[3a] in the course of the structure proof of fusidic acid and has been used in our laboratories as an entry to the novel 4,8,14-trimethyl-18-norandrostane series.[2b] At the outset of our work on the degradation of fusidic acid we found that in addition to the expected products (**3**), ozonolysis led to a new series of compounds whose structure and reactions are the basis of this paper. The starting materials used in this work consist of a variety of fusidic acid derivatives[1,2] which were prepared by standard procedures described in the Experimental Section.

When methyl $3\alpha,16\beta$-diacetoxy-11-keto-$\Delta^{17(20)}$-fusiden-21-oate (**2b**) was ozonized in glacial acetic acid at 10–15° rather than by the previously described[3a] conditions (at −70° in methylene chloride containing 1% pyridine), a crystalline product was isolated in 40% yield. The elemental analysis for this compound showed that it contained one more oxygen than expected product **3a**. On the basis of the analytical data and the spectral and chemical data to be described, this compound has been assigned structure **4a**. Its infrared spectrum showed the presence of four carbonyl functions at 5.62 (3-acetate), 5.67 (16-acetate), 5.78 (17a-carbonyl), and 5.88 μ (11-carbonyl). In addition, the nmr spectrum showed a single proton appearing as a triplet J = 6.5–7 cps centered at τ 3.54. This peak at low field indicates a proton attached to carbon bearing two oxygen functions and is reminiscent of that found by Lavie and co-workers[4] in the ring A lactol acetate **5** derived from euphol. In **5** the proton at C-1 resonates as a single peak at τ 3.58.

Subsequent to the isolation of the lactol acetate **4a** from the ozonolysis of **2b** in acetic acid, we found that it was also formed during ozonolysis using Godtfredsen's conditions. Although expected diacetoxy diketone **3a** could not itself be isolated from the ozonolysis reaction, its presence in at least 30% yield was shown by its reductive deacetoxylation with zinc in refluxing acetic acid to the known[2a] acetoxy diketone **6a**. In addition to **6a**, lactol acetate **4a** (unaffected by the zinc–acetic acid treatment) was isolated from this reaction in 5% yield.

Similar results to those described above were obtained from ozonolysis of 3-keto compounds. Thus, when 3,11-diketone **1b** derived from fusidic acid, or its methyl ester (**1c**), was ozonized in acetic acid, a 30–35% yield of the lactol acetate **4b** was obtained. This compound had a peak at τ 7.84 in the nmr spectrum (16β-acetate protons) and the 16α proton appeared as a multiplet centered at τ 3.54. When the ozonolysis was carried out in methylene chloride, known acetoxy triketone **3b** was obtained in 46% yield. Godtfredsen reports[3a] that this compound has a melting point of 211.5–212.5°. We have found that the melting range of acetoxy triketone, isolated in different runs and having identical infrared spectra, varied from 184–186° to 224–226°. It is our belief that small amounts of lactol acetate **4b**, mp 255–257°, in these samples are responsible for the variable melting point behavior,

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(1) A preliminary report on this work was presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Abstracts, p 20P.

(2) (a) Paper I: P. A. Diassi, G. W. Krakower, I. Bacso, and H. A. Van Dine, *Tetrahedron*, **22**, 3443 (1966). (b) Paper II: P. A. Diassi, I. Bacso, G. W. Krakower, and H. A. Van Dine, *ibid.*, **22**, 3459 (1966).

(3) (a) W. O. Godtfredsen and S. Vangedal, *ibid.*, **18**, 1029 (1962); (b) W. O. Godtfredsen, W. von Daehne, S. Vangedal, A. Marquet, D. Arigoni, and A. Melera, *ibid.*, **21**, 3505 (1965).

(4) D. Lavie, E. Glotter, and Y. Shvo, *ibid.*, **19**, 1377 (1963).