12-Hydroxydodec-3Z-enoic Acid (IV). Under the conditions described in the preparation of the hydroxyalkenoic acid (III), 0.31 g ($1.46 \cdot 10^{-3}$ mole) of the hydroxyalkynoic acid (XVIII) yielded 0.29 g (93% of the acid (IV) in the form of a colorless oil, R_f 0.32 [hexane–diethyl ether (1:4)]. IR spectrum (ν, cm^{-1}): 730, 1660 and 3015 (Z–CH=CH), 1715 and 2400-3600 (CO_2H, OH). PMR spectrum (100 MHz, $CDCl_3$): 1.15-1.75 (m, 12H, CH_2), 1.9-2.15 (m, 2H, H-5), 3.12 (d, 2H, J = 5.1 Hz, H-2), 3.65 (t, 2H, J = 6.3 Hz, H-12), 5.5-5.7 (m, 2H, H-3, H-4), see [5].

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INSECT PHEROMONES AND THEIR ANALOGUES

XL. SYNTHESIS OF DODEC-3Z-EN-11RS-OLIDE (FERRULACTONE II – A RACEMIC ANALOGUE OF A COMPONENT OF THE AGGREGATION PHEROMONE OF Cryptolestes ferrugineus

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UDC 542.91+547.473+632.936.2

A new route, based on the partial ozonolysis of ω-acetyl derivatives of alk-1-en-4-ynes, is proposed for the synthesis of 11RS-hydroxydodec-3Z-enoic acid, the cyclization of which gives dodec-3Z-en-11RS-olide (ferrulactone II) – a racemic analogue of one of the macrolide components of the aggregation pheromone of the rust-red grain beetle.

Synthesis of optically active dodec-3Z-en-11-olide (I) – one of the macrolide components of a pheromone of the rust-red grain beetle (cryptolestes ferrugineus) – have been described [1-3]. Since, however, the racemic macrolide (I) is also biologically active [4-6], its synthesis is also of practical significance. The (±)-11-hydroxydodec-3Z-enoic acid (II)

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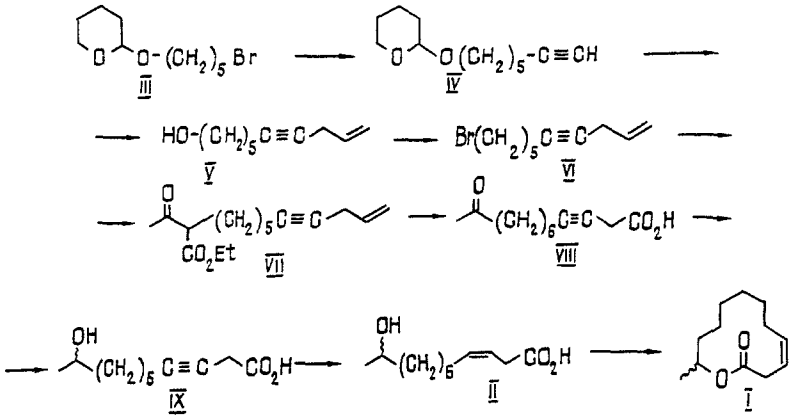
Translated from Khimiya Prirodnykh Soedinenii, Nos. 3,4, pp. 423-429, May-August, 1992. Original article submitted October 8, 1991.

0009-3130/92/0304-0369$12.50

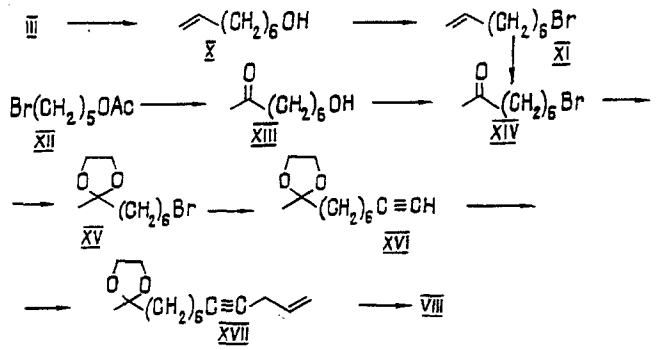
required for cyclization to the macrolide (I) has been obtained previously via the corresponding ω-alkoxyallenecarboxylic acid [7].

We have developed a new approach to the synthesis of the hydroxy acid (II) based on the partial ozonolysis of ω-acetyl derivatives of alk-1-en-4-ynes. This approach has been realized by two routes. In the first, 3-ethoxycarbonyl-2-oxotridec-12-en-9-yne (VII) served as the enynic compound: its ozonolysis, followed by the Jones oxidation of the peroxide product and de-ethoxycarbonylation led to 11-oxododec-3-ynoic acid (VIII). Reduction of the latter with the aid of sodium tetrahydroborate gave racemic 11-hydroxydodec-3-ynoic acid (IX) the catalytic hydrogenation of which completed the synthesis of the (Z)-hydroxy acid (II). Cyclization of the latter under conditions that we have described previously [2] gave the desired macrolide (I), which is known in the literature under the name ferrulactone II.



The ketoenyne (VII) was obtained by condensing the enynic bromide (VI) with acetoacetic ester, the starting compound in this scheme being the readily accessible [8] bromohydrin ether (III), converted into the bromide (VI) in three stages [via the intermediate alkyne (IV) and the alkenyne (V)].

In the second route, the starting compound was either the same ether (III) or the acetoxy bromide (XII), either of which was converted into 2-bromo-8-oxooctane (XIV). As the overall yield of the bromo ketone (XIV) from ether (III) through the intermediate oct-7-en-1-ol (X) and the bromide (XI) proved to be lower than from the bromo acetate (XII) via the intermediate hydroxy ketone (XIII) (39.5 and 47.5%, respectively), it is preferable to start from compound (XII). The subsequent transformations of the keto bromide (XIV) in the form of an acetal derivative (XV) led via the intermediate alkyne (XVI) to the enyne (XVII), the ozonolysis of which gave the alkynic keto acid (VIII), identical with that obtained by the first proposed scheme.



The overall yield of the desired ferrulactone (II) calculated on the initial acetoxy bromide (XII) was 2.9%, which somewhat exceeds the yields achievable from the THP ether (III) via either of the bromides (VI) and (XI) (2.7 and 2.4%, respectively).

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in films), and MR spectra were recorded on a Tesla BS-567 instrument (working frquency 100 MHz). With $CDCl_3$ as the solvent, the chemical shifts being given on the δ scale relative to the signal of TMS (internal standard). GLC analysis was conducted on a Chrom-5 instrument with, as the stationary phase,

the silicone liquid SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm) at working temperatures of 50-300°C, the carrier gas being helium. TLC was performed on Silufol-brand plates with a fixed layer of silica gel. The analyses of the compounds synthesized agreed with the calculated figures.

1-(Tetrahydropyran-2yloxy)hept-6-yne (IV). Acetylene was passed at the rate of 1 liter/min for 1 h at −35°C through a stirred suspension of lithium amide obtained from 1.2 g (0.17 g-atom) of lithium. 0.1 g $FeCl_3$, and 200 ml of redistilled liquid ammonia, and, after 15 min, a solution of 18.9 g ($75.3 \cdot 10^{-3}$ mole) of 1-bromo-5-(tetrahydropyran-2-yl)pentane (III) [8] in 36 ml of a mixture (1:1 by volume) of abs. THF and DMSO was added, and the reaction mixture was stirred at the same temperature for 4 h; then the ammonia was evaporated off, and the residue was diluted with 50 ml of water and was extracted with pentane (3 × 300 ml). The extract was washed successively with water, 10% HCl, and saturated solutions of $NaHCO_3$ and NaCl, and was dried with $MgSO_4$, and evaporated. The residue was chromatographed [SiO_2, hexane–diethyl ether (9:1)], to give 12.7 g (86%) of (IV), n_D^{22} 1.4751, R_f 0.67 [hexane–diethyl ether (3:1)]. PMR spectrum (100 MHz, $CDCl_3$): 1.4-1.7 (m, 12H, CH_2O), 1.91 (t, 1H, J = 2.5 Hz, H-7), 2.1 (m, 2H, H-5), 3.3-3.9 (m, 4H, CH_2O), 4.56 (br. s 1H, OCHO), see [9].

Dec-9-en-6-yn-1-ol (V). A solution of 29.8 g (0.15 mole) of compound (IV) in 30 ml of abs. THF was added after 20 min to a stirred (20°C, Ar) suspenesion of EtMgBr obtained from 3.65 g (0.15 g-atom) of magnesium and 18.3 g (0.17 mole) of EtBr in 50 ml of abs. diethyl ether. The mixture was boiled for 3.5 h and was then treated at 0°C with 28.91 g (0.15 mole) of CuI and was stirred at 20°C for 0.5 h, after which 27.58 g (0.23 mole) of allyl bromide was added. The reaction mixture was stirred at 20°C for 12 h and was then treated with a saturated solution of NH_4Cl and was extracted with diethyl ether (3 × 200 ml). The extract was evaporated, the residue was dissolved in 340 ml of methanol containing 6.8 g of TsOH, and the solution was stirred at room temperature for 24 h and was then concentrated in vacuum. The concentrate was diluted with diethyl ether and was washed successively with saturated solutions of $NaHCo_3$ and NaCl, dried with $MgSO_4$ and evaporated, and the residue was distilled, to give 20.3 g (89%) of the alcohol (V), bp 114-115°C (4 mm), n_D^{23} 1.4941 [2]. IR spectrum (ν, cm^{-1}): 920, 990, 1645 and 3090 ($CH{=}CH_2$), 2230 ($C{\equiv}C$), 1060 (C–O), 3350 (OH). PMR spectrum (100 MHz, $CDCl_3$): 1.5-1.7 (m, 6H, CH_2), 2.2 (m, 2H, H-5), 2.9-3.0 (m, 2H, H-8), 3.64 (t, 2H, J = 7 Hz, H-1), 5.0-5.4 (m, 2H, H-10), 5.65-6.05 (m, 1H, H-9).

1-Bromodec-9-en-6-yne (VI). A suspension of 25.4 g ($96.8 \cdot 10^{-3}$ mole) of Ph_3P and 15.5 g ($96.8 \cdot 10^{-3}$ mole) of Br_2 in 120 ml of CCl_4 was stirred at 0°C for 0.5 h, and then 12.3 g ($80.8 \cdot 10^{-3}$mole) of the hydroxyenyne (V) was added. After 3 h, the mixture was diluted with 300 ml of pentane, filtered through a layer of SiO_2 (150 g) and evaporated in vacuum. This gave 14.3 g (82%) of the bromide (VI), n_D^{23} 1.5077 [2]. IR spectrum (ν, cm^{-1}): 570 and 650 (C–Br), 930, 1000, 1640 and 3090 ($CH{=}CH_2$), 2230 ($C{\equiv}C$). PMR spectrum (100 MHz $CDCl_3$): 1.5-1.9 (m, 6H, CH_2), 2.2 (m, 2H, H-5), 2.9-3.0 (m, 2H, H-8), 3.41 (t, 2H, J = 6.5 Hz, H-1), 5.0-5.4 (m, 2H, H-10), 5.7-6.0 (m, 1H, H-9).

11-Ethoxycarbonyl-12-oxotridec-1-en-4-yne (VII). To a solution of sodium ethanolate obtained by dissolving 0.32 g ($14 \cdot 10^{-3}$ g-aom) of sodium in 70 ml of abs. ethanol was added 2.0 g ($14 \cdot 10^{-3}$ mole) of acetoacetic ester, the mixture was heated to the boil, 2.14 g ($10 \cdot 10^{-3}$ mole) of the bromide (VI) was added dropwise, and boiling was continued for another 6 h; then, after cooling to room temperature, the solution was decanted off and the residue was washed by decantation with 10 ml of abs. ethanol. The combined solution was evaporated and the residue was chromatographed (SiO_2, hexane–diethyl ether (7:3), to give 1.76 g (67%) of the keto ester (VII), n_D^{23} 1.4750. IR spectrum (ν, cm^{-1}): 910, 990, 1645 and 3085 ($CH{=}CH_2$), 2220 ($C{\equiv}C$), 1245 and 1740 (CO_2Et), 1715 (C=O). PMR spectrum (100 MHz $CDCl_3$): 1.28 (t, 3H, J = 7 Hz, CH_3CH_2O), 1.2-1.7 (m, 8H, CH_2), 2.2 (m, 2H, H-8), 2.23 (s, 3H, H-1), 2.85-3.0 (m, 2H, H-11), 3.40 (t, 1H, J = 7.3 Hz, H-3), 4.17 (q, 2H, J = 7 Hz, CH_3CH_2O), 5.0-5.4 (m, 2H, H-13), 5.65-6.1 (m, 1H, H-12).

Oct-7-en-1-ol (X). A suspension of 5.27 g ($27.6 \cdot 10^{-3}$ mole) of CuI in 100 ml of abs. THF was treated with 4.3 g ($27.6 \cdot 10^{-3}$ mole) of 2,2'-bipyridyl and the mixture was stirred for 0.5 h (20°c, Ar); it was then cooled to 2°C and was treated with 9.66 g ($79.8 \cdot 10^{-3}$ mole) of allyl bromide in 15 ml of abs. THF, and the resulting mixture was stirred for 10 min. Then the Grignard reagent obtained from 1.77 g ($72.8 \cdot 10^{-3}$ g-atom) of magnesium and 16.65 g ($66.5 \cdot 10^{-3}$ mole) of 1-bromo-5-(tetrahydropyran-2-yloxy)pentane in 50 ml of abs. THF was added and the reaction mixture was stirred at 2°C for 4 h and at 20°C for 15 h; after this, 50 ml

of saturated NH_4Cl solution ws added and it was stirred for another 1 h and was extracted with diethyl ether (3 × 250 ml). The extract was evaporated, the residue was dissolved in 250 ml of methanol containing 1.0 g of TsOH, and, after being stirred at room temperature for 24 h, the solution was concentrated in vacuum. The residue was diluted with 0.5 liter of diethyl ether, and the solution was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$ and evaporated, and the residue was distilled, to give 5.9 g (70%) of the alcohol (X), bp 64-66°C (7 mm) (see [10]), its IR and PMR spectra being identical with those described in [11].

1-Bromooct-7-ene (XI). At −5 to 0°C, 9.16 g ($48 \cdot 10^{-3}$ mole) of p-toluenesulfonyl chloride was added in portions to a solution of 5.12 g ($40 \cdot 10^{-3}$ mole) of the alcohol (X) in 14.5 ml of dry pyridine, and the reaction mixture was stirred at −5°C for 6 h and was kept at 0°C for 12 h; it was then poured onto ice (~20 g) and extracted with diethyl ether (3 × 100 ml). The ethereal solution was washed successively with 10% HCl and with saturated solutions of $NaHCO_3$ and NaCl and was dried with $MgSO_4$ and evaporated. The residue (a tosylate, 10.7 g) was dissolved in 75 ml of abs. DMFA and was treated with 12.6 g (0.123 mole) of NaBr; the mixture was heated at 65°C for 2 h and was then cooled to room temperature, and, after the addition of 10 ml of water, it was extracted with pentane (3 × 100 ml), and the combined extracts were washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. The residue was chromatographed (SiO_2, pentane) and yielded 6.3 g (82%) of bromide (XI), n_D^{21} 1.4693, IR and PMR spectra identical with those described in [10].

1-Hydroxyoctan-7-one (XIII). Acetoacetic ester (22.1 g; 0.17 mole) was added to a solution of sodium ethanolate obtained from 3.91 g (0.17 g-atom) of sodium and 85 ml of abs. ethanol, the mixture was heated to the boil, and 35.5 g (0.17 mole) of 1-acetoxy-5-bromopentane (XII) [12] was added; the resulting mixture was boiled for 8 h and was then cooled to room temperature, the solution was decanted off, the residue was washed with 20 ml of ethanol, and the combined solutions were evaporated. The residue (33 g) was treated with 340 g of 5% NaOH, the mixture was stirred at room temperature for 15 h and was extracted with diethyl ether (3 × 50 ml), and the aqueous layer was treated with 48 g of 50% H_2SO_4 and was boiled for 2 h. The reaction mixture was extracted with diethyl ether (3 × 200 ml), and the extract was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with Na_2SO_4, and evaporated, to give 17.0 g (69%) of the keto alcohol (XIII), n_D^{22} 1.4485, its IR and PMR spectra being identical with those described in]13].

1-Bromooctan-7-one (XIV). As described from bromide (XI), 12.7 g ($88.2 \cdot 10^{-3}$ mole) of the alcohol (XIII) and 20.45 g (0.107 mole) of p-toluenesulfonyl chloride in 30 ml of dry pyridine gave 20.0 g of the intermediate tosylate, part (17.9 g) of which was dissolved in 100 ml of abs. DMFA and was treated with 20.03 g (0.195 mole) of NaBr; under the conditions described for the bromide (XI), 11.3 g (69%) of the keto bromide (XIV) was obtained; n_D^{20} 1.4768; its IR and PMR spectra were identical with those described in [14].

b) A mixture of 0.53 g ($3 \cdot 10^{-3}$ mole) of $PdCl_2$, 2.97 g ($30 \cdot 10^{-3}$ mole) of CuCl, 14 ml of DMFA, and 2 ml of water was stirred in an atmosphere of oxygen for 1 h, and then a solution of 5.73 g ($30 \cdot 10^{-3}$ mole) of the bromide (XI) in 7 ml of DMFA and 1 ml of water was added. The reaction mixture was stirred (O_2) for 24 h, and then 100 ml 3 N HCl was added and it was extracted with diethyl ether (5 × 150 ml); the extract was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$ and evaporated. The residue was chromatographed [SiO_2, hexane–diethyl ether (1:1)], giving 4.3 g (69%) of the bromo ketone (XIV), identical with that obtained in the preceding experiment.

1-Bromo-7,7-ethylenedioxyoctane (XV). A mixture of 11.1 g ($53.6 \cdot 10^{-3}$ mole) of the bromo ketone (XIV), 4 g of ethylene glycol, 0.29 g of Py·TsOHY, and 36 ml of abs. benzene was boiled in a flask fitted with a Dean–Stark trap until the evolution of water had ceased (~35 h), and it was then diluted with 300 ml of diethyl ether and was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated. The residue was chromatographed [SiO_2, hexane–diethyl ether (4:1)], giving 10.9 g (81%), of the acetal (XV), n_D^{20} 1.4773. IR spectrum (ν, cm^{-1}): 560 and 640 (C–Br), 1040, 1070 and 1120 (C–O–C). PMR spectrum (100 MHz, $CDCl_3$): 1.31 (s, 3H, H-8), 1.3-1.9 (m, 10H, CH_2), 3.41 (t, 2H, J = 6.5 Hz, H-1), 3.93 (s, 4H, OCH_2CH_2O).

9,9-Ethylenedioxydec-1-yne (XVI). Acetylene was passed at the rate of 1 liter/min for 0.3 h at −35°C through a stirred suspension of lithium amide obtained from 0.32 g ($45.8 \cdot 10^{-3}$ g-atom) of lithium and 0.02 g of $FeCl_3$ in 100 ml of redistilled liquid ammonia, after which

a solution of 9.2 g ($36.7 \cdot 10^{-3}$ mole mole) of the bromide (XV) in 9.2 ml of abs. THF and 9.2 ml of abs. DMSO was added; the reaction mixture was stirred at the same temperature for 4.5 h, and then the ammonia was evaporated off and the residue was diluted with water and extracted with hexane (3 × 150 ml). The extract was washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated. The residue was chromatographed [SiO_2, hexane–diethyl ether (3:1)], giving 6.6 g (83%) of the alkyne (XVI). IR spectrum (ν, cm^{-1}): 2130 and 3320 (C≡CH), 1050, 1090 and 1130 (C–O–C). PMR spectrum (100 MHz, $CDCl_3$): 1.31 (s, 3H, H-1), 1.3-1.75 (m, 10H, CH_2), 1.93 (t, 1H, J = 2.5 Hz, H-10), 2.05-2.28 (m, 2H, H-8), 3.93 (s, 4H, OCH_2CH_2O).

12,12-Ethylenedioxytridec-1-en-4-yne (XVII). A solution of 6.6 g ($33.7 \cdot 10^{-3}$ mole) of the alkyne (XVI) in 8 ml of abs. THF was added to a stirred S(20°C, Ar) suspension of EtMgBr obtained from 0.82 g ($33.7 \cdot 10^{-3}$ g-atom) of magnesium and 3.82 g ($35 \cdot 10^{-3}$ mole) of EtBr in 12 ml of abs. diethyl ether. The mixture was boiled for 3.5 h, and was cooled to 0°C and treated with 6.42 g ($33.7 \cdot 10^{-3}$ mole) of CuI; it was then stirred at 20°C for 0.5 h, after which 6.12 g ($50.6 \cdot 10^{-3}$ mole) of allyl bromide was added. The reaction mixture was stirred at 20°C for 12 h and was then treated with a saturated solution of NH_4Cl and was extracted with diethyl ether (3 × 100 ml). The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated, and the residue was distilled, to give 5.9 g (74%) of the enyne (XVII), bp 129-131°C (3 mm). IR spectrum (ν, cm^{-1}): 920, 1000, 1645 and 3090 (CH=CH_2), 1050, 1085 and 1130 (C–O–C), 2220 (C≡C). PMR spectrum (100 MHz, $CDCl_3$), 1.31 (s, 3H, H-1), 1.3-1.75 (m, 10H, CH_2), 2.2 (m, 2H, H-8), 2.86-3.0 (m, 2H, H-11), 3.93 (s, 4H, OCH_2CH_2O), 50-5.4 (m, 2H, H-13), 5.6-6.0 (m, 1H, H-12).

11-Oxododec-3-ynoic Acid (VIII). a) A mixture of ozone and oxygen (5.5 wt. % of O_3) was passed at the rate of 30 liters/h through a solution of 1.32 g ($5.0 \cdot 10^{-3}$ mole) of compound (VII) in 20 ml of cyclohexane and 1.6 ml of AcOH at 5°C until 0.24 g ($5.0 \cdot 10^{-3}$ mole) of O_3 had been absorbed. The product was purged with Ar, the solvent was decanted off, the residue was dissolved in acetone, and the solution was treated dropwise at 0°C with 0.7 ml ($5.6 \cdot 10^{-3}$ mole) of a 8 N solution of H_2CrO_4; the mixture was stirred for 0.5 h and was then warmed to 20°C and stirred for another 4 h, and, after the addition of 0.5 ml of isopropanol (to decompose the excess of oxidant), it was evaporated in vacuum, and the residue was diluted with 5 ml of water and was extracted with diethyl ether (3 × 50 ml). The extract was treated with a saturated solution of $NaHCO_3$ to pH 8, the aqueous layer was separated off and was acidified with 10% HCl to pH ≤ 3 and extracted with diethyl ether (3 × 50 ml), and the extract was dried with $MgSO_4$ and evaporated. To a solution of the residue (0.93 g) in 8 ml of DMSO were added 0.55 g ($13 \cdot 10^{-3}$ mole) of LiCl and 0.12 g ($6.5 \cdot 10^{-3}$ mole) of water and the mixture was heated at 170°C for 0.5 h, cooled to 0°C, diluted with diethyl ether (100 ml), washed with a cooled saturated solution of NaCl (3 × 10 ml) dried with $MgSO_4$, and evaporated. The residue was chromatographed [SiO_2, petroleum ether–diethyl ether (2:3)] and yielded 0.28 g (27%) of the acid (VIII) in the form of a colorless oil, R_f 0.28 [petroleum ether–diethyl ether (2:3)]. PMR spectrum (100 MHz, $CDCl_3$): 1.15-1.75 (m, 8H, CH_2), 2.06 (s, 3H, H-12), 1.95-2.6 (m, 4H, H-5, H-10), 3.31 (t, 2H, J = 2.5 Hz, H-2), see [1].

b) A mixture of ozone and oxygen (5.5 wt. % of O_3) was passed at the rate of 30 liters/h through a solution of 2.36 g ($10.0 \cdot 10^{-3}$ mole) of compound (XVII) in 35 ml of cyclohexane and 3.5 ml of AcOH at 5°C until 0.48 g ($10 \cdot 10^{-3}$ mole) of O_3 had been absorbed. The mixture was purged with Ar, the solvent was decanted off, the residue was dissolved in 20 ml of acetone; this solution was treated dropwise at 0°C with 1.4 ml ($11.2 \cdot 10^{-3}$ mole) of a 8N solution of H_2CrO_4, and the resulting mixture was warmed for 0.5 h to 20°C and stirred for another 4 h, after which 1 ml of isopropanol was added and it was evaporated in vacuum. The residue was dissolved in 10 ml of water and extracted with diethyl ether (4 × 50 ml). The extract was treated with a saturated solution of $NaHCO_3$ to pH 8, the aqueous layer was separated off, acidified with 10% HCl to pH ≤ 3, and extracted with diethyl ether (3 × 100 ml), and the extract was evaporated. The residue was dissolved in a mixture of 30 ml of acetone and 1 ml of 10% HCL, and the solution was stirred at 20°C for 6 h and was then evaporated; the new residue was extracted with diethyl ether (3 × 100 ml), and the extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. This gave 1.09 g (52%) of the acid (VIII), identical with that obtained in the preceding experiment.

11RS-Hydroxydodec-3-ynoic Acid (IX). At 0°C, 0.25 g ($6.5 \cdot 10^{-3}$ mole) of $NaBH_4$ was added to a solution of 0.68 g ($3.2 \cdot 10^{-3}$ mole) of the keto acid (VIII) in 10 ml of abs. ethanol;

after the reaction mixture had been stirred for 10 min, it was treated with 5% HCl that had been cooled to 0°C and was extracted with diethyl ether (3 × 70 ml). The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. This gave 0.58 g (85%) of the hydroxy acid (IX) in the form of a colorless oil, R_f 0.30 [hexane–diethyl ether (1:4)]. PMR spectrum (100 MHz, $CDCl_3$): 1.19 (d, 3H, J = 7 Hz, H-12), 1.3-1.7 (m, 10H, CH_2), 2.2 (m, 2H, H-5), 3.31 (t, 2H, J = 2.5 Hz, H-2), 3.8 (m, 1H, H-11), see [3].

11RS-Hydroxydodec-3Z-enoic Acid (II). A suspension of 0.31 g ($8.2 \cdot 10^{-3}$ mole) of $NaBH_4$ and 0.4 ml ($0.8 \cdot 10^{-3}$ mole) of a 2 N solution of NaOH in 8 ml of ethanol was stirred at 20°C for 15 min and was then filtered, and 2.4 ml of the filtrate was added after 10 min to a suspension of 0.48 g ($1.9 \cdot 10^{-3}$ mole) of $Ni(OAc)_2 \cdot 4H_2O$ in 10 ml of ethanol that was being stirred in an atmosphere of H_2. The resulting mixture was treated with 0.34 ml ($3.1 \cdot 10^{-3}$ mole) of ethylenediamine and was left for 5 min, and then 0.31 g ($1.46 \cdot 10^{-3}$ mole) of compound (IX) in 3 ml of ethanol was added. The reaction mixture was stirred at 20°C for 2 h, and it was then diluted with saturated NaCl solution and extracted with diethyl ether (3 × 50 ml). The usual working up of the extract yielded 0.29 g (93%) of the acid (II) in the form of a colorless oil, R_f 0.34 [hexane–diethyl ether (1:4)]. PMR spectrum (100 MHz, $CDCl_3$): 2.20 (d, 3H, J = 7 Hz, H-12), 1.3-1.7 (m, 10H, CH_2), 1.9-2.2 (m, 2H, H-5), 3.11 (d, 2H, J = 5.4 Hz, H-2), 3.8 (m, 1H, H-11), 5.5-5.7 (m, 2H, H-3, H-4), see [3].

Dodec-3-en-11RS-olide (I). A solution of 0.3 g ($1.4 \cdot 10^{-3}$ mole) of the hydroxy acid (II), 0.64 g ($2.9 \cdot 10^{-3}$ mole) of 2,2'-dipyridyl disulfide, and 0.76 g ($2.9 \cdot 10^{-3}$ mole) of PPh_3 in 18 ml of MeCN was kept at 20°C for 2 h and was then worked up as described in [2]. This gave 0.082 g (30%) of compound (I), n_D^{20} 1.4780, R_f 0.59 [hexane–diethyl ether (1:1)], IR spectrum identical with that given in [2].

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