2-Hept-2-en-1-ol (VI). The compound consists of a mixture of Z and E isomers (3.3-4.3: 1). PMR spectrum of a mixture of Z and E isomers: 0.9 m, 1.35 m, 2.03 m (9H, C^7–C^4), 1.92 s (1H, OH), 4.06 d (J_1 = 5.0, 2H, C^1 Z isomer), 4.17 d (2H, C^1, E isomer, J_2 = 5.5); 5.64 m (1H, C^3). ^{13}C NMR spectrum: 13.7 (C^7), 22.1 (C^6), 31.2 (C^5), 31.8 (C^4), 63.1 and 58.0 (C^1), 128.9 and 126 (C^2), 132.7 and 125 (C^3). Mass spectrum, m/z (I, %): 114 (I) [M^+], 96 (10), 81 (21), 68 (16), 67 (13), 57 (100), 55 (34), 54 (22), 44 (18), 43 (31), 41 (71).

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EFFICIENT SYNTHESIS OF 3E,13Z-OCTADECADIENOL, ITS ACETATE, 4E,6E,11Z-HEXADECATRIENAL, AND 4E,6E,11Z-HEXADECATRIENYL ACETATE, SEX PHEROMONES OF SOME LEPIDOPTERAN SPECIES

N. M. Ivanova, B. A. Cheskis, A. M. Moiseenkov, and O. M. Nefedov

UDC 541.63:542.91:547.315.2:632.78

The title linear acetogenins have been synthesized by a strategy of joining acetylcyclopropane to 8Z-tridecenol or 5Z-decenol prepared after Julia, leading to the corresponding secondary cyclopropylcarbinols. The $ZnBr_2/Me_3SiBr$-initiated homoallylic rearrangement of the latter assures at a key step the stereospecific construction of transoid fragments of the target molecules.

The vast majority of known acetogenic lepidopteran pheromones belong to the linear oligoolefins, for which the construction strategy consists mainly of selective reductive transformation of the appropriate acetylenic precursors or the Wittig–Schlosser [1] olefination of carbonyl compounds. Recently we proposed a new approach to the stereospecific synthesis of transoid members of this class of bioregulators, based on the use of readily available acetylcyclopropane derivatives and the homoallylic rearrangement of the corresponding cyclopropylcarbinols initiated by zinc halides in the presence of trimethylsilylhalides [2, 3]. Further possibilities of the method are illustrated in the present communication, with a route to E,Z-di- and E,E,Z-trienyl acetogenic compounds (I)-(IV), in which the cisoid C=C bond of both pairs has been formed by olefination of the selected aldehyde synthons after Julia [4].

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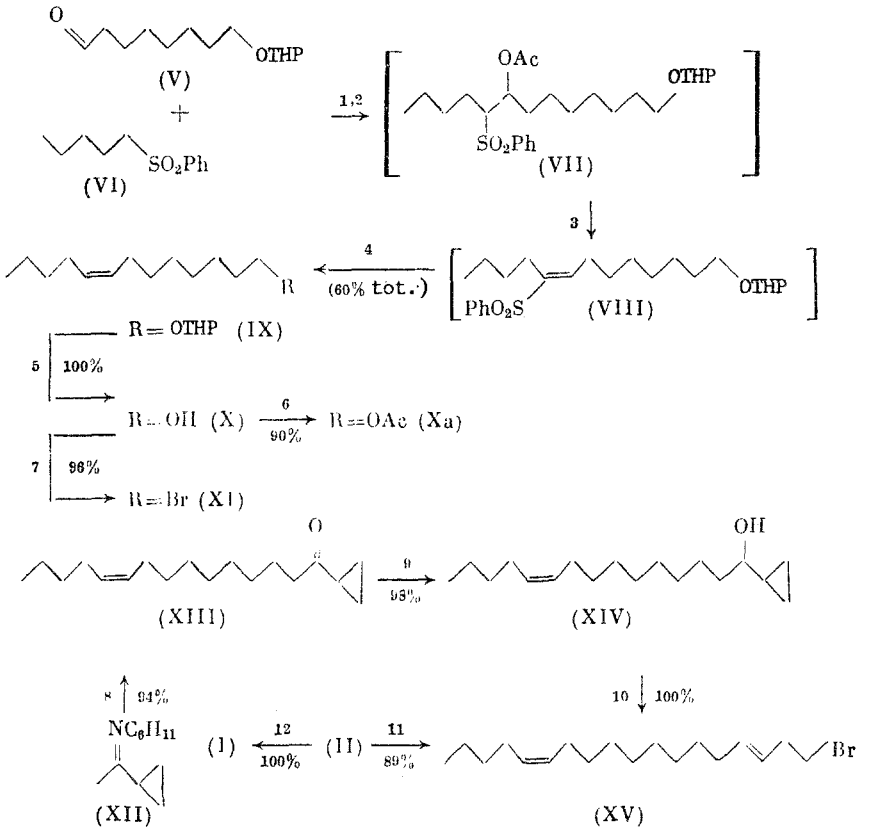
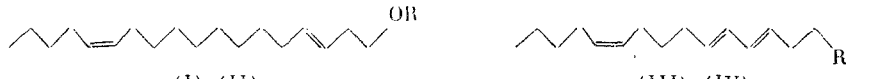
0568-5230/91/4011-2196$12.50

Scheme 1



Reagents and conditions: 1) n-BuLi, hexane, THF, −10°C, 30 min; 2) Ac_2O, 4-dimethylaminopyridine (DMAP) (cat.), 25°C, 20 min; 3) NaOH, Et_2O, MeOH (cat.), 25°C, 20 min; 4) $Na_2S_2O_4$, $NaHCO_3$, EtOH, H_2O, 80°C, 7 h; 5) TsOH·Py (cat.), MeOH, 50°C, 2 h; 6) Ac_2O, DMAP (cat.), Py, 0°C, 20 min; 7) a: n-BuLi, Ph_3CH (cat.), hexane, Et_2O, HMPTA, −30°C, then TsCl, 25°C, 15 min; b: NaBr, DMF, 50°C, 1 h; 8) LDA, hexane, THF, 0°C, 45 min, then (XI), −70°C → 25°C, 15 min, then SiO_2, 25°C, 15 min; 9) $LiAlH_4$, Et_2O, 0°C, 15 min; 10) Me_3SiBr, $ZnBr_2$ (cat.), CH_2Cl_2, −20°C, 15 min; 11) AcOK, dibenzo-18-crown-6 (DB-18-C-6) (cat.), MeCN, 80°C, 15 h; 12) NaOH, MeOH, H_2O, 25°C, 15 min.



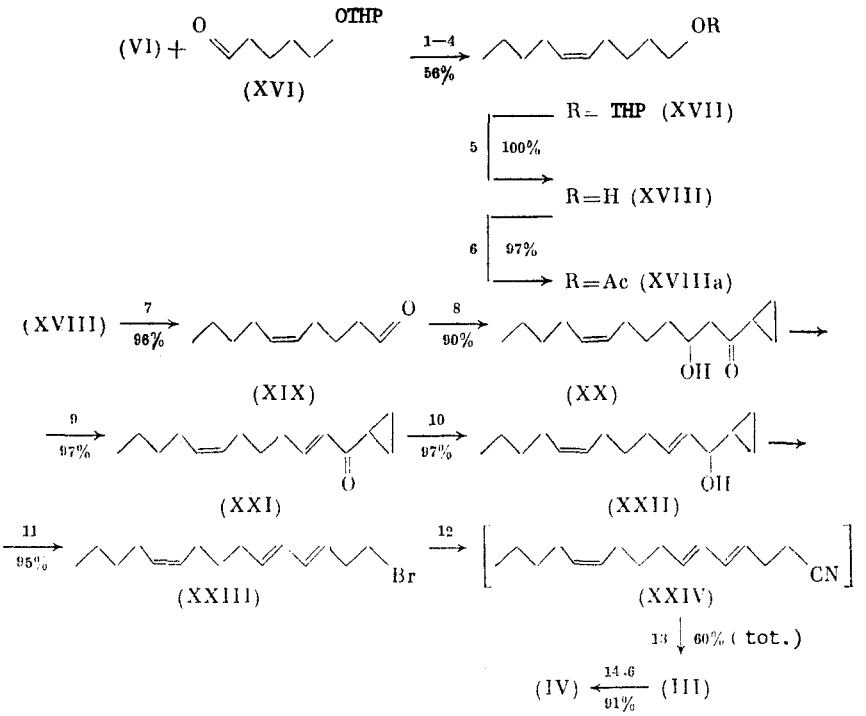
(I), (II) (III), (IV)

R = H (I), Ac (II), CHO (III), CH_2OAc (IV).

The components of the first pair, 3E,13Z-octadecadienol (I) and its acetate (II) are sex pheromones (SP) of the aergerlid moths Paranthrene tabaniformis [5] and Synthanedon pictipes [6], respectively. A mixture of these dienes serves additionally as a sex attractant (SA) for the insects Synanthedon bibionipennis [7] and Pennisetia hylaeformis [8]. The synthesis of these acetogenins was carried out (Scheme 1) by joining C_{13} and C_5 fragments, the first of which, Z-olefin (XI), was prepared from tetrahydropyranyl (THP) ether (V) [9] and sulfone (VI).

Condensation of (VI), deprotonated with strong base, with (V) (the corresponding aldol proved inefficient), conversion of the adduct to acetate (VII), elimination of AcOH, and desulfonation of (VIII) with sodium dithionite gave, without intermediate purification of the sulfones (VII) and (VIII), olefin (IX) in overall 60% yield. The slowest transformation in this sequence of Julia [4] is the reaction yielding the vinylsulfone, whose completion in the case of (VIII) under the recommended conditions (powdered alkali in anhydrous ether) requires ~24 h. We found that the use of catalytic amounts of MeOH at this step

Scheme 2



Reagents and conditions: 1-6) identical to these positions in Scheme 1; 7) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, $-60°C \rightarrow -15°C$, 1.5 h; 8) (XII), LDA, hexane, THF, $-10°C$, 20 min, then SiO_2, 25°C, 10 min; 9) $TsOH \cdot H_2O$ (cat.), PhH, 80°C, 15 min; 10) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, MeOH, $-40°C$, 10 min; 11) Me_3SiBr, $ZnBr_2$ (cat.), CH_2Cl_2, $-20°C$, 15 min; 12) KCN, DB-18-C-6 (cat.), MeCN, 80°C, 12 h; 13) i-Bu_2AlH, PhMe, hexane, $-70°C$, 40 min; 14) $LiAlH_4$, Et_2O, 0°C, 15 min.

sharply accelerated the reaction and led to full conversion of acetate (VII) in only ~20 min. Removal of the ether (IX) protecting group yielded quantitatively 8Z-tridecenol (X), whose acetate (Xa) is known to be a SP component for the insects Chilo auricilius [10] and Plusia chalcites [11]. Alcohol (X) may in turn be converted to intermediate C_{13} bromide (XI) with equal efficiency.

In accordance with the methodology developed in our laboratory [3], the terminal step of the synthesis of E,Z-dienes (I) and (II) consisted of the initial low-temperature alkylation by bromide (XI) of N-cyclohexylimine acetylcyclopropane (XII), chosen as a C_5 fragment of the target molecules, in the form of its Li derivative, readily obtained by treatment with lithium diisopropylamide (LDA). The resulting cyclopropylketone (XIII) reduced readily to alcohol (XIV). Cyclopropylcarbinyl rearrangement of the latter, initiated by $ZnBr_2$ in the presence of Me_3SiBr as in [2], gave in quantitative yield homoallylbromide (XV), acetolysis of which gave in high yield the target pheromone (II), saponified in the final step to dienol (I) (Scheme 1).

The components of the other pair, 4E,6E,11Z-hexadecatrienal (III) and the related acetate (IV) have recently been identified as SP components of the saturniid Samia cynthia ricini [12]. Their synthesis was carried out (Scheme 2) by a $C_{10} + C_5 + C_1$ assembly, where the second fragment is the previous imine (XII), while the first, Z-enal (XIX) is readily prepared from sulfone (VI) and the available [13] aldehyde ether (XVI).

Julia addition of (VI) and (XVI) under the conditions described above smoothly gave THP ether (XVII), which was quantitatively transformed to 5Z-decenol (XVIII), a SA for the insect Coleophora laricella [14]. The corresponding acetate (XVIIIa) is a known SP component of a widespread pest of numerous agricultural crops, the fall cutworm Agrotis segetum [15], and of the insect Argyrogramma verruca [16].

Swern oxidation [17] of (XVIII) gave the intermediate C_{10} aldehyde (XIX), whose controlled condensation with the carbanion generated from imine (XII) as in [3] gave in high

yield β-ketol (XX), readily dehydrated to dienone (XXI). Hydride reduction by $NaBH_4/CeCl_3$ [18] led almost quantitatively to allylcyclopropylcarbinol (XXII), which under the conditions adopted for the related alcohol (XIV) underwent rapid rearrangement to C_{15} homoallylbromide (XXIII). The final step in the synthesis of the target structure consisted first of C_1 homologation of (XXIII) to the intermediate nitrile (XXIV) which without further purification was smoothly converted by hydride reduction to trienal (III), from which in turn two standard operations yielded the acetate (IV).

The structures of all synthesized compounds were reliably demonstrated spectrally and confirmed, for the known dienes (I), (II) [19] and olefins (X) [20], (XVIII) [21], (XVIIIa) [15], and (XIX) [22], by comparison of physicochemical characteristics with published values. A comparative analysis of ^{13}C NMR spectra for Z-olefins (X) and (XVIII) and their already known E isomers [3] revealed, in agreement with available data for 1,2-dialkylsubstituted E/Z-alkenes [23], a displacement of the alkyl carbon signals of the first pair, $\delta \approx 27$ ppm, to higher field by $\Delta\delta \approx 5$ ppm. The signal intensities agree with the >97% stereochemical purity of the Z-alcohols determined by capillary GLC. This is true also for the E fragments of compounds (I)-(IV), (XV), and (XXI)-(XXIII), whose PMR spectra display couplings of J = 15-16 Hz, typical of vicinal protons for the corresponding C=C bonds.

The schemes presented have thus led to the stereospecific synthesis of SPs (I), (II) and (III), (IV) with overall yields of ~45% and ~25%, respectively.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument in $CHCl_3$ solution, UV spectra of ethanolic solutions on a Specord UV-VIS spectrophotometer. ^1H and ^{13}C NMR spectra were taken in $CDCl_3$ relative to TMS on Bruker WM-250 and AM-300 instruments, respectively (working frequency for carbon, 75 MHz). Mass spectra were acquired at 70 eV ionization potential on a Varian MAT CH-6. GLC was performed on LKhM-80 (column 3 m × 3 mm with 15% Carbowax 20 M on N-AW-DMCS packing) and Biokhrom (capillary column 50 m × 0.2 mm with OV-275) chromatographs.

1-(2-Tetrahydropyranyloxy)-8Z-tridecene (IX). To a stirred solution at −70°C under Ar of 1.89 g (8.92 mmoles) of (VI) [24] in 30 ml THF and 2 ml HMPTA over 15 min were added 4.7 ml of a 1.81 M solution of n-BuLi (8.51 mmoles) in hexane. The mixture was held for 30 min at −15°C, then chilled to −70°C and treated for 10 min with a solution of 1.94 g (8.51 mmoles) of (V) [9] in 10 ml THF, and stirred 30 min at −10°C, then 0.1 g (0.82 mmole) of DMAP and 1.3 g (12.74 mmoles) of Ac_2O were added. The reaction mixture was warmed for 30 min to 25°C, stirred for 20 min, diluted with water, and extracted with ether. The extract was washed with saturated NaCl solution and dried with $MgSO_4$, the ether was removed under vacuum, and to 4.48 g of the residue in 60 ml ether was added 0.68 g (17.0 mmoles) of powdered NaOH and 0.6 ml MeOH. The resulting suspension was stirred under Ar for 20 min at 25°C, filtered through a layer (~3 cm) of SiO_2, and concentrated under vacuum. A solution of the residue (3.41 g) in 100 ml of 50% aqueous ethanol containing 4.44 g (25.52 mmoles) of $Na_2S_2O_4$ and 4.29 g (51.07 mmoles) of $NaHCO_3$ was refluxed for 7 h and then extracted with ether. The extract was washed with water, then saturated NaCl solution, dried with $MgSO_4$, and concentrated under vacuum and the residue (2.48 g) was chromatographed on 70 g of SiO_2. Gradient elution from hexane to ether (to 5% of the latter) gave 1.44 g (60%) of (IX) as a colorless oil, n_D^{24} 1.4589. IR spectrum (ν, cm^{-1}): 790, 870, 905, 970, 1030, 1075, 1120, 1135, 1235, 1255, 1275, 1320, 1350, 1380, 1440, 1450, 1465, 2860, 2915, 3000. PMR spectrum (δ, ppm; J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.9 m (20H, CH_2), 1.9-2.1 m (4H, HC^7, HC^{10}), 3.3-3.9 m (4H, OCH_2), 4.58 br.t (1H, OCHO, J = 4), 5.25-5.45 m (2H, HC^8, HC^9). Mass spectrum, m/z (I, %): 209 (2), 207 (4), 127 (7), 111 (9), 101 (7), 97 (11), 96 (13), 91 (16), 85 (100), 69 (25), 67 (25), 57 (21), 55 (45), 44 (25), 43 (23), 41 (37). Found, %: C 76.12, H 12.2. $C_{18}H_{34}O_2$. Calculated, %: C 76.54, H 12.13.

8Z-Tridecenol-1 (X). A solution of 3.36 g (11.91 mmoles) of (IX) and 0.3 g (1.2 mmoles) of TsOH·Py [25] in 50 ml MeOH was heated for 2 h at 50°C and then concentrated under vacuum. The residue (3 g) was chromatographed on 60 g of SiO_2. Gradient elution from hexane to ether (to 10% of the latter) gave 2.36 g (100%) of (X) [20], bp 91°C (0.02 mm), n_D^{23} 1.4539. PMR spectrum (δ, ppm; J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.6 m (14H, CH_2), 1.9-2.1 m (4H, HC^7, HC^{10}), 3.65 t (2H, HC^1, J = 7), 5.25-5.45 m (2H, HC^8, HC^9). ^{13}C NMR spectrum (δ, ppm): 13.92 (C^{13}), 22.29 (C^{12}), 25.67 (C^3), 26.87 and 27.11 (C^7 and C^{10}), 29.27 and 29.64 (C^4, C^5, and C^6), 31.92 (C^{11}), 32.73 (C^2), 62.99 (C^1), 129.79 and 129.94 (C^8 and

C^9). ^{13}C NMR of 8E-tridecenol [3] (δ, ppm): 13.90 (C^{13}), 22.14 (C^{12}), 25.69 (C^3), 29.25, 29.38, and 29.54 (C^4, C^5, and C^6), 31.80 (C^{11}), 32.23 and 32.52 (C^7 and C^{10}), 32.73 (C^2), 62.92 (C^1), 130.21 and 130.35 (C^8 and C^9).

Acetate (Xa), yield 90%, bp 90°C (0.015 mm), n_D^{24} 1.4448. IR spectrum (ν, cm^{-1}): 970, 1040, 1210, 1260, 1370, 1390, 1440, 1470, 1735, 2870, 2940, 2970, 3010. PMR spectrum (δ, ppm; J, Hz), 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (12H, CH_2), 1.62 br.quint (2H, HC^2, J = 7), 1.9-2.1 m (4H, HC^7, HC^{10}), 2.06 s (3H, CH_3CO), 4.06 t (2H, HC^1, J = 7), 5.30-5.45 m (2H, HC^8, HC^9). Mass spectrum, m/z (I, %): 180 (20), 124 (15), 123 (15), 110 (30), 109 (25), 96 (85), 95 (56), 82 (65), 81 (80), 69 (30), 68 (45), 67 (90), 55 (100), 54 (50), 43 (70), 41 (5). Found, %: C 75.10, H 11.82. $C_{15}H_{28}O_2$. Calculated, %: C 74.95, H 11.74.

1-Bromo-8Z-tridecene (XI). To a solution of 1.93 g (9.75 mmoles) of (X) and 10 mg of Ph_3CH in 40 ml ether and 3 ml DMF, stirred at −30°C under Ar, was added a 1.5 M solution of BuLi in hexane until a stable pink color formed (~6.5 ml; 9.75 mmoles), after which 1.99 g (10.45 mmoles) of TsCl was added in a single portion. The mixture was stirred 15 min at 25°C, then diluted with water and extracted with ether. The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and concentrated under vacuum. A solution of the residue (3.5 g) in 40 ml DMF containing 4.02 g (39.03 mmoles) NaBr, was heated 1 h at 50°C, diluted with water and extracted with hexane. The extract was dried with $MgSO_4$ and concentrated under vacuum and the residue redistilled. Product was 2.43 g (96%) of (XI), bp 96°C (0.02 mm), n_D^{22} 1.4702. IR spectrum (ν, cm^{-1}): 560, 645, 710, 970, 1200, 1245, 1300, 1375, 1435, 1460, 2860, 2930. PMR spectrum (δ, ppm; J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.5 m (12H, CH_2), 1.86 quint (2H, HC^2, J = 7), 1.9-2.1 m (4H, HC^7, HC^{10}), 3.41 t (2H, HC^1, J = 7), 5.30-5.45 m (2H, HC^8, HC^9). Mass spectrum, m/z (I, %): M^+ 262 (32) and 260 (30), 165 (26), 163 (28), 150 (40), 148 (42), 112 (26), 97 (74), 83 (74), 70 (94), 69 (98), 67 (100), 57 (45), 56 (55), 55 (43), 54 (40), 43 (30), 41 (68). Found, %: C 60.16, H 9.74, Br 30.22. $C_{13}H_{25}Br$. Calculated, %: C 59.77, H 9.65, Br 30.58.

1-Cyclopropyl-10Z-pentadecenone-1 (XIII). To a 1.85 M solution of BuLi (4.7 ml, 8.7 mmoles) in hexane stirred at −30°C under Ar was added over 5 min a solution of 0.92 g (9.11 mmoles) i-Pr_2NH in 4 ml THF. The mixture was held 15 min at 0°C and then treated at −30°C with 1 ml HMPTA and a solution of 1.51 g (9.15 mmoles) of (XII) [26] in 4 ml THF. The reaction mixture was stirred for 45 min at 0°C and chilled to −70°C and treated for 5 min with a solution of 2.17 g (8.31 mmoles) of (XI) in 6 ml THF. The mixture was warmed to 25°C over 20 min, diluted with water within 15 min, and extracted with ether. The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and concentrated under vacuum and the residue (3 g) was mixed with 8 g SiO_2 (silica gel L 100/60), held 15 min at 25°C, and then loaded onto 60 g SiO_2 and chromatographed. Gradient elution from hexane to ether (to 3% of the latter) gave 2.06 g (94%) of (XIII) as a colorless oil, n_D^{21} 1.4642. IR spectrum (ν, cm^{-1}): 665, 725, 880, 905, 970, 1060, 1205, 1390, 1455, 1680, 2860, 2930, 3000, 3090. PMR spectrum (δ, ppm; J, Hz): 0.8-1.1 m (7H, CH_3, cyclopropyl CH_2), 1.2-1.4 m (14H, CH_2), 1.6 m (2H, HC^3), 1.9-2.1 m (5H, CH, HC^9, HC^{12}), 2.53 t (2H, HC^2, J = 7), 5.30-5.45 m (2H, HC^{10}, HC^{11}). Mass spectrum, m/z (I, %): M^+ 264 (6), 178 (10), 151 (11), 137 (5), 123 (6), 108 (7), 97 (45), 84 (79), 69 (100), 55 (98), 41 (72). Found, %: C 81.87, H 12.51. $C_{18}H_{32}O$. Calculated, %: C 81.75, H 12.20.

1-Cyclopropyl-10Z-pentadecenol-1 (XIV). To a suspension of 0.25 g (6.58 mmoles) of $LiAlH_4$ in 15 ml ether stirred at 0°C under Ar was added over 15 min a solution of 1.71 g (6.48 mmoles) of (XIII) in 5 ml ether. Within 10 min the mixture was treated successively with 0.3 ml water, 0.3 ml of a 15% aqueous solution of KOH, and 0.9 ml water, dried with $MgSO_4$, and concentrated under vacuum. Yield 1.69 g (98%) of (XIV) as a colorless oil, n_D^{22} 1.4661. IR spectrum (ν, cm^{-1}): 665, 725, 825, 880, 920, 970, 1050, 1205, 1380, 1410, 1460, 2860, 2930, 3080, 3450, 3600. PMR spectrum (δ, ppm; J, Hz); 0.2-0.6 m (4H, cyclopropyl CH_2), 0.8-1.0 m (4H, CH_3, CH), 1.2-1.7 m (18H, CH_2), 1.9-2.1 m (4H, HC^9, HC^{12}), 2.86 br.q (1H, HC^1, J = 7), 5.30-5.45 m (2H, HC^{10}, HC^{11}). Mass spectrum, m/z (I, %): 248 (6), 204 (6), 134 (5), 121 (6), 110 (9), 109 (10), 96 (12), 95 (11), 82 (12), 81 (14), 71 (100), 69 (13), 67 (13), 55 (33), 43 (38), 41 (41). Found, %: C 81.51, H 12.83. $C_{18}H_{34}O$. Calculated, %: C 81.13, H 12.86.

1-Bromo-3E,13Z-octadecadiene (XV). To a suspension of 1.59 g (5.98 mmoles) of (XIV) and 0.3 g (1.33 mmoles) $ZnBr_2$ in 35 ml CH_2Cl_2, stirred at −20°C under Ar, was added over 5 min a solution of 2.01 g (13.14 mmoles) of Me_3SiBr in 10 ml of CH_2Cl_2. The reaction mixture was stirred for 15 min at −20°C and treated with a saturated aqueous solution of $NaHCO_3$

and extracted with ether. The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and concentrated under vacuum and the residue (2 g) chromatographed on 30 g SiO_2 (hexane elution). Yield 1.96 g (100%) of (XV) as a colorless oil, n_D^{22} 1.4790. IR spectrum (ν, cm^{-1}): 565, 645, 670, 730, 880, 970, 1050, 1205, 1255, 1270, 1380, 1390, 1430, 1460, 2860, 2930. PMR spectrum (δ, ppm; J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (16H, CH_2), 1.9-2.1 m (6H, HC^5, HC^{12}, HC^{15}), 2.55 br.q (2H, HC^2, J = 7), 3.37 t (2H, HC^1, J = 7), 5.30-5.45 m (3H, HC^3, HC^{13}, HC^{14}), 5.55 br.dt (1H, HC^4, J = 15 and 7). Mass spectrum, m/z (I, %): M^+ 230 (41) and 228 (38), 191 (23), 160 (25), 158 (21), 121 (21), 107 (36), 95 (32), 94 (58), 93 (51), 81 (66), 80 (66), 79 (83), 67 (55), 66 (62), 65 (83), 55 (100), 54 (62), 41 (62). Found, %: C 65.45, H 10.38, Br 24.60. $C_{18}H_{33}Br$. Calculated, %: C 65.64, H 10.10, Br 24.26.

3E,13Z-Octadecadienyl Acetate (II). A mixture of 1.05 g (3.19 mmoles) of (XV), 1.56 g (15.92 mmoles) of AcOK, and 20 mg (0.056 mmole) DB-18-C-6 in 60 ml MeCN was refluxed 15 h, then filtered, the filtrate concentrated under vacuum, and the residue (1 g) chromatographed on 20 g of SiO_2. Gradient elution from hexane to ether (to 5% of the latter) gave 0.87 g (89%) of (II) [19] as a colorless oil, n_D^{23} 1.4570. PMR spectrum (δ, ppm; J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (16H, CH_2), 1.9-2.1 m (6H, HC^5, HC^{12}, HC^{15}), 2.06 s (3H, CH_3CO), 2.32 br.q (2H, HC^2, J = 7), 4.07 t (2H, HC^1, J = 7), 5.28-5.33 m (3H, HC^3, HC^{13}, HC^{14}), 5.52 br.dt (1H, HC^4, J = 15 and 7).

1-(2-Tetrahydropyranyloxy)-5Z-decene (XVII). As described above for (IX), from 8.68 g (40.9 mmoles) of (VI), 27.3 ml of a 1.43 M solution of BuLi (39.0 mmoles) in hexane, 7.25 g (39.0 mmoles) of (XVI) [13] in 70 ml THF and 5 ml HMPTA, and then 5.96 g (58.4 mmoles) of Ac_2O and 0.48 g (3.9 mmoles) of DMAP was obtained 21.06 g of the intermediate acetoxysulfone, which was treated with 3.12 g (78 mmoles) of powdered NaOH and 1 ml MeOH in 100 ml ether. The vinylsulfone thus prepared (15.02 g) was desulfonylated with 20.35 g (0.117 mole) $Na_2S_2O_4$ and 19.65 g (0.234 mole) $NaHCO_3$ in 0.4 liter of boiling 50% aqueous ethanol. Product 5.23 g (56%) of (XVII) as a colorless oil, n_D^{22} 1.4581. IR spectrum (ν, cm^{-1}): 795, 870, 905, 970, 985, 1030, 1075, 1120, 1135, 1175, 1255, 1350, 1440, 1465, 2860, 2920, 3000. PMR spectrum (δ, ppm; J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.9 m (14H, CH_2), 1.9-2.1 m (4H, HC^4, HC^7), 3.3-3.9 m (4H, OCH_2), 4.58 br.t (1H, OCHO, J = 4), 5.30-5.45 m (2H, HC^5, HC^6). Mass spectrum, m/z (I, %): M^+ 240 (0.7), 167 (2), 136 (6), 97 (15), 95 (17), 85 (100), 84 (28), 83 (31), 81 (25), 69 (45), 67 (59), 57 (54), 55 (100), 45 (86), 43 (59), 41 (100). Found, %: C 74.68, H 11.49. $C_{15}H_{28}O_2$. Calculated, %: C 74.95, H 11.74.

5Z-Decenol-1 (XVIII). Analogously as described for (IX), from 2.46 g (10.25 mmoles) of (XVII) and 0.26 g (1.04 mmoles) of TsOH·Py in 50 ml MeOH was obtained 1.6 g (100%) of (XVIII) [21], bp 92°C (1 mm), n_D^{21} 1.4515. PMR spectrum (δ, ppm; J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.7 m (8H, CH_2), 1.9-2.1 m (4H, HC^4, HC^7), 3.65 t (2H, HC^1, J = 7), 5.3-5.5 m (2H, HC^5, HC^6. ^{13}C NMR spectrum (δ, ppm): 13.86 (C^{10}), 22.26 (C^9), 25.65 (C^3), 26.87 (C^4 and C^7), 31.86 (C^8), 32.23 (C^2), 62.47 (C^1), 129.37 and 130.22 (C^5 and C^6). ^{13}C NMR of 5E-decenol (δ, ppm): 13.90 (C^{10}), 22.15 (C^9), 25.69 (C^3), 31.77 (C^8), 32.23 (C^4 and C^7), 32.35 (C^2), 62.89 (C^1), 129.75 and 130.86 (C^5 and C^6).

Acetate (XVIIIa) [15], yield 97%, bp 80°C (1 mm), n_D^{20} 1.4400. PMR spectrum (δ, ppm: J, Hz): 0.89 t (3H, CH_3, J = 7), 1.2-1.7 m (8H, CH_2), 1.9-2.1 m (4H, HC^4, CH^7), 2.05 s (3H, CH_3CO), 4.06 t (2H, HC^1, J = 7), 5.30-5.45 m (2H, HC^5, HC^6).

5Z-Decenal (XIX). To a solution of 2.57 g (20.24 mmoles) of $(COCl)_2$ in 35 ml CH_2Cl_2 stirred at −60°C under Ar was added over 5 min a solution of 2.33 g (29.87 mmoles) of DMSO in 15 ml CH_2Cl_2. The mixture was held 15 min at −60°C, then treated for 20 min with a solution of 1.37 g (8.78 mmoles) of (XVIII) in 40 ml CH_2Cl_2 and, within 40 min, with 7.14 g (70.69 mmoles) Et_3N. The reaction mixture was stirred 45 min at −15°C, then decomposed with 35 ml 1 M HCl and extracted with ether. The extract was washed with saturated $NaHCO_3$ and NaCl solutions, dried with $MgSO_4$, and concentrated under vacuum, and the residue (2 g) chromatographed on 40 g SiO_2. Gradient elution from hexane to ether (to 2% of the latter) gave 1.3 g (96%) of (XIX) [22], bp 52°C (1 mm), n_D^{20} 1.4442. PMR spectrum (δ, ppm; J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (4H, HC^8, HC^9), 1.70 quint (2H, HC^3, J = 7), 1.9-2.1 m (4H, HC^4, HC^7), 2.45 t.d (2H, HC^2, J = 7 and 2), 5.25-5.50 m (2H, HC^5, HC^6), 9.77 t (1H, HC^1, J = 2).

1-Cyclopropyl-3-hydroxy-7Z-dodecenone-1 (XX). To a solution of LDA prepared from 4.4 ml of a 1.85 M solution of BuLi (8.14 mmoles) in hexane and 0.87 g (8.61 mmoles) of i-Pr_2NH in 4 ml THF, stirred at −30°C under Ar, was added over 5 min a solution of 1.41 g (8.55 mmoles) of (XII) in 4 ml THF. The mixture was held 45 min at 0°C and then cooled to −70°C,

treated for 5 min with a solution of 1.2 g (7.79 mmoles) of (XIX) in 4 ml THF, and stirred 20 min at −10°C, after which it was diluted with water and extracted with ether. The extract was concentrated under vacuum and the residue (2.8 g) mixed with 7 g SiO_2, held 10 min at 25°C, and then loaded onto 40 g SiO_2 and chromatographed. Gradient elution from hexane to ether (to 20% of the latter) gave 1.72 g (93%) of (XX), bp 108°C (0.02 mm), n_D^{20} 1.4748. IR spectrum (ν, cm^{-1}): 660, 700, 710, 815, 840, 905, 975, 1025, 1080, 1110, 1195, 1210, 1310, 1395, 1460, 1690, 2870, 2940, 2960, 3010, 3100, 3530, 3670. PMR spectrum (δ, ppm; J, Hz): 0.8-1.1 m (4H, cyclopropyl CH_2), 0.88 t (3H, CH_3, J = 7), 1.2-1.6 m (8H, CH_2), 1.9 m (1H, CH), 1.9-2.1 m (4H, HC^6, HC^9), 2.71 part of AB spectra of ABX (δ_A = 2.66, δ_B = 2.76, J_{AB} = 18, J_{AX} = 9, J_{BX} = 3, 2H, HC^2), 3.22 br.d (1H, OH, J = 3), 4.02 m (1H, HC^3), 5.25-5.45 m (2H, HC^7, HC^8). Mass spectrum, m/z (I, %): M^+ 238 (1), 220 (4), 136 (17), 126 (19), 110 (39), 95 (25), 84 (23), 82 (23), 81 (53), 69 (100), 68 (46), 67 (42), 55 (51), 54 (55), 43 (46), 41 (94). Found, %: C 75.45, H 11.06. $C_{15}H_{26}O_2$. Calculated, %: C 75.58, H 10.99.

1-Cyclopropyl-2E,7Z-dodecadienone-1 (XXI). A solution of 1.48 g (6.22 mmoles) of (XX) and 50 mg $TsOH \cdot H_2O$ in 25 ml benzene was refluxed with a Dean–Stark attachment until evolution of water ceased (~15 min), then washed with saturated $NaHCO_3$ and NaCl solutions, dried with $MgSO_4$, and concentrated under vacuum, and the residue redistilled. Yield 1.33 g (97%) of (XXI), bp 135°C (0.03 mm), n_D^{20} 1.4865. IR spectrum (ν, cm^{-1}): 620, 685, 815, 890, 910, 975, 1030, 1060, 1090, 1190, 1235, 1280, 1310, 1390, 1440, 1625, 1660, 1680, 2860, 2930, 2960, 3000, 3095. UV spectrum (λ_{max}, nm): 228 (ε 18,200). PMR spectrum (δ, ppm; J, Hz): 0.8-1.1 m (4H, cyclopropyl CH_2), 0.89 t (3H, CH_3, J = 7), 1.2-1.4 m (4H, HC^{10}, HC^{11}), 1.55 quint (2H, HC^5, J = 7), 1.9-2.3 m (7H, CH, HC^4, HC^6, HC^9), 5.3-5.5 m (2H, HC^7, HC^8), 6.23 br.d (1H, HC^2, J = 16), 6.92 d.t (1H, HC^3, J = 16 and 7). Mass spectrum, m/z (I, %): M^+ 220 (2), 177 (7), 163 (10), 152 (12), 136 (44), 123 (42), 121 (20), 95 (65), 92 (23), 81 (69), 79 (46), 69 (61), 55 (100), 53 (29), 44 (29), 43 (37), 41 (28). Found, %: C 81.50, H 11.07. $C_{15}H_{24}O$. Calculated, %: C 81.76, H 10.98.

1-Cyclopropyl-2E,7Z-dodecadienol-1 (XXII). To a solution of 1.3 g (5.91 mmoles) of (XXI) and 2.2 g (5.91 mmoles) of $CeCl_3 \cdot 7H_2O$ in 25 ml MeOH stirred at −40°C under Ar was added in portions 0.22 g (5.79 mmoles) of $NaBH_4$. The reaction mixture was stirred 10 min at −40°C and then diluted with water and extracted with a mixture of ether:hexane (1:1). The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and concentrated under vacuum and the residue was redistilled. Yield 1.27 g (97%) of (XXII), bp 110°C (0.015 mm), n_D^{20} 1.4765. IR spectrum (ν, cm^{-1}): 690, 795, 825, 870, 920, 970, 1000, 1025, 1050, 1090, 1235, 1380, 1435, 1460, 1670, 2860, 2880, 2930, 2960, 3010, 3080, 3550, 3600. PMR spectrum (δ, ppm; J, Hz): 0.2-0.6 m (4H, cyclopropyl CH_2), 0.90 t (3H, CH_3, J = 7), 0.9-1.1 m (1H, CH), 1.2-1.4 m (4H, HC^{10}, HC^{11}), 1.46 quint (2H, HC^5, J = 7), 1.9-2.1 m (6H, HC^4, HC^6, HC^9), 3.45 br.t (1H, HC^1, J = 7), 5.25-5.45 m (2H, HC^7, HC^8), 5.55 d.d.d (1H, HC^2, J = 16, 7, and 3), 5.66 d.t.d (1H, HC^3, J = 16, 7, and 3). Mass spectrum, m/z (I, %): 204 (3), 136 (19), 123 (21), 107 (24), 97 (28), 95 (46), 93 (29), 91 (33), 83 (29), 82 (35), 81 (62), 79 (80), 69 (100), 67 (80), 55 (97), 43 (73), 41 (58). Found, %: C 80.70, H 11.70. $C_{15}H_{26}O$. Calculated, %: C 81.02, H 11.79.

1-Bromo-3E,5E,10Z-pentadecatriene (XXIII). As described above for (XIV) from 0.4 g (1.8 mmoles) of (XXII), 0.61 g (3.99 mmoles) of Me_3SiBr, and 90 mg (0.4 mmole) of $ZnBr_2$ in 40 ml of CH_2Cl_2 was obtained 0.49 g (95%) of (XXIII) as a colorless oil, n_D^{21} 1.5102. IR spectrum (ν, cm^{-1}): 640, 685, 960, 985, 1020, 1040, 1260, 1370, 1450, 1650, 2850, 2920, 2950, 2995, 3070. UV spectrum (λ_{max}, nm): 233 (ε 23,300). PMR spectrum (δ, ppm; J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (4H, HC^{13}, HC^{14}), 1.45 quint (2H, HC^8, J = 7), 1.9-2.2 m (6H, HC^7, HC^9, HC^{12}), 2.63 br.q (2H, HC^2, J = 7), 3.40 t (2H, HC^1, J = 7), 5.25-5.45 m (2H, HC^{10}, HC^{11}), 5.53 d.t (1H, HC^3, J = 15 and 7), 5.66 d.t (1H, HC^6, J = 15 and 7), 5.9-6.2 m (2H, HC^4, HC^5). Mass spectrum, m/z (I, %): M+ 286 (1.5) and 284 (1.2), 229 (2), 227 (2), 205 (2), 203 (2), 121 (8), 119 (7), 107 (12), 105 (12), 95 (20), 93 (20), 91 (27), 81 (37), 79 (46), 69 (29), 67 (51), 55 (63), 44 (100), 41 (78). Found, %: C 62.74, H 8.92, Br 28.29. $C_{15}H_{25}Br$. Calculated, %: C 63.16, H 8.83, Br 28.01.

4E,6E,11Z-Hexadecatrienal (III). A suspension of 0.49 g (1.72 mmoles) of (XXIII), 0.44 g (6.77 mmoles) of KCN, and 60 mg (0.17 mmole) of DB-18-C-6 in 7 ml MeCN was refluxed 12 h, then filtered and the filtrate concentrated under vacuum. To a stirred solution of the residue (0.39 g) in 14 ml hexane at −70°C under Ar was added over 5 min 2.53 ml of a 1 M solution of i-Bu_2AlH (2.53 mmoles) in toluene. The reaction mixture was stirred 40 min at −70°C, then decomposed with 3% HCl and extracted with ether. The extract was washed with saturated $NaHCO_3$ and NaCl solutions, dried with Na_2SO_4, and concentrated under vacuum, and the residue (0.3 g) chromatographed on 8 g SiO_2. Gradient elution from hexane to ether

(to 2% of the latter) gave 0.24 g (60%) of (III) as a colorless oil, n_D^{20} 1.4931. IR spectrum (ν, cm^{-1}): 660, 695, 865, 900, 950, 975, 995, 1055, 1105, 1210, 1260, 1310, 1360, 1380, 1390, 1410, 1440, 1460, 1560, 1580, 1625, 1660, 1730, 2740, 2870, 2940, 3020. UV spectrum (λ_{max}, nm): 232 (ε 22,000). PMR spectrum (δ, ppm; J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (4H, HC^{14}, HC^{15}), 1.43 quint (2H, HC^9, J = 7), 1.9-2.2 m (6H, HC^8, HC^{10}, HC^{13}), 2.40 br.q (2H, HC^3, J = 7), 2.56 t.d (2H, HC^2, J = 7 and 2), 5.25-5.45 m (2H, HC^{11}, HC^{12}), 5.55 d.t (1H, HC^4, J = 15 and 7), 5.61 d.t (1H, HC^7, J = 15 and 7), 5.9-6.1 m (2H, HC^5, HC^6), 9.79 t (1H, HC^1, J = 2). Mass spectrum, m/z (I, %): M^+ 234 (0.6), 190 (1), 159 (1), 150 (24), 137 (24), 135 (24), 134 (28), 121 (34), 119 (40), 107 (25), 95 (55), 94 (26), 93 (52), 92 (23), 91 (45), 82 (49), 81 (100), 80 (48), 79 (96), 77 (29), 69 (32), 68 (26), 57 (21), 55 (67), 41 (67). Found, %: C 81.69, H 10.96. $C_{16}H_{26}O$. Calculated, %: C 81.99, H 11.18.

4E,6E,11Z-Hexadecatrienyl Acetate (IV). To a stirred solution of 0.13 g (0.56 mmole) of (III) in 5 ml ether at 0°C under Ar was added in one portion 10 mg (0.26 mmole) of $LiAlH_4$. The reaction mixture was stirred 15 min at 0°C and further treated as described above for (XIII). To 0.13 g of separated product in 1 ml pyridine at 0°C was added 10 mg (0.08 mmole) of DMAP and 0.1 g (0.98 mmole) of Ac_2O. The mixture was held for 20 min at 0°C, then diluted with ether, washed with 3% HCl, saturated $NaHCO_3$ and NaCl solutions, dried with Na_2SO_4, concentrated under vacuum, and the residue (0.15 g) chromatographed on 6 g SiO_2. Gradient elution from hexane to ether (to 2% of the latter) gave 0.14 g (91%) of (IV) as a colorless oil, n_D^{20} 1.4833. IR spectrum (ν, cm^{-1}): 605, 635, 880, 950, 65,* 995, 1040, 1210, 1255, 1370, 1390, 1435, 1735, 2860, 2940, 2970, 3010. UV spectrum (λ_{max}, nm): 232 (ε 30,500). PMR (δ, ppm; J, Hz): 0.91 t (3H, CH_3, J = 7), 1.2-1.4 m (4H, HC^{14}, HC^{15}), 1.45 quint (2H, HC^9, J = 7), 1.74 quint (2H, HC^2, J = 7), 1.9-2.2 m (8H, CH_2), 2.08 s (3H, CH_3CO), 4.09 t (2H, HC^1, J = 7), 5.25-5.45 m (2H, HC^{11}, HC^{12}), 5.55 d.t (1H, HC^4, J = 15 and 7), 5.60 d.t (1H, HC^7, J = 15 and 7), 5.9-6.1 m (2H, HC^5, HC^6). Mass spectrum, m/z (I, %): M^+ 278 (11), 161 (25), 147 (26), 121 (29), 120 (28), 119 (38), 107 (31), 105 (48), 95 (35), 94 (31), 93 (54), 91 (58), 82 (31), 81 (61), 80 (60), 79 (100), 67 (60), 55 (51), 43 (65), 41 (41). Found, %: C 77.96, H 10.74. $C_{18}H_{30}O_2$. Calculated, %: C 77.65, H 10.86.

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