Chemistry of Natural Compounds and Bioorganic Chemistry

Pheromones of Coleoptera

13.* Synthesis of racemic ferrulactone II from three easily accessible acetylenic precursors

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A ten-step synthesis of a racemic form of 3(*Z*),11(*S*)-dodecen-11-olide (ferrulactone II) has been developed. The synthesis is based on the Cadiot—Chodkiewicz cross-coupling of 4-pentyn-2-ol with 2-propyn-1-ol followed by carbon chain elongation by 3-butyn-1-ol and gives the target lactone in 9.7 % overall yield (based on the starting pentynol). All of the three building blocks used for the chain assembly are easily accessible from acetylene. The protection of OH groups as *tert*-butyl ethers has certain synthetic advantages.

Key words: (±)-3(*Z*)-dodecen-11-olide, synthesis; terminal alkynes, cross-coupling and *C*-alkylation; *tert*-butyl ethers, synthetic application.

Multicomponent sex pheromones of some species of grain beetles of the *Cucujidae* family contain chiral and achiral unsaturated macrocyclic lactones, the structure of which is characterized by the presence of a 3(*Z*)-olefin or 3(*Z*),6(*Z*)-diene fragment.[2—5] One of these compounds, 3(*Z*),11(*S*)-dodecen-11-olide (ferrulactone II), is the main component of the aggregation pheromone of *Cryptolestes ferrugineus* (Stephens), and has become an object of extensive synthetic investigations.[6—13] The most important stage in the synthesis of ferrulactone II and related biologically active macrolides is the preparation of the key intermediate, β,γ-*cis*-ω-hydroxyalkenoic (alkadienoic) acid, which is preferably built from acetylenic precursors[6—11] or by the Wittig reaction.[12,13]

The present work considers a "modified acetylenic" strategy in which simple and easily accessible C_5, C_4, and C_3 ynols are used as the starting compounds, and the *tert*-butyl group is employed to protect the alcoholic functions in the course of the synthesis.

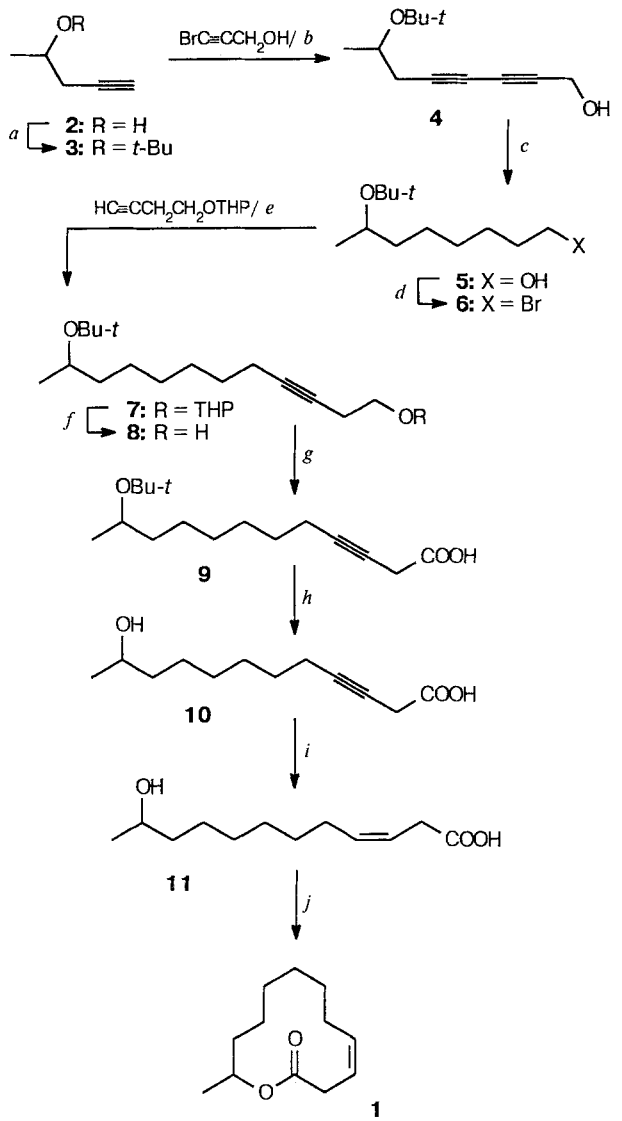
The method proposed by us for the preparation of racemic 3(*Z*)-dodecen-11-olide (**1**), which also exhibits attractant activity with respect to *C. ferrugineus* (Scheme 1), makes use of 4-pentyn-2-ol (**2**) as the starting compound. Compound **2** is easily converted into the corresponding *tert*-butyl ether (**3**). Cross-coupling of ether **3** with 3-bromo-2-propyn-1-ol according into Cadiot—Chodkiewicz[14] occurs with a high yield. It is followed by a two-step transformation of the resulting conjugated diynol (**4**) into the saturated C_8 bromide (**6**),

* For part 12, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2122—2125, December, 1993.

1066-5285/93/4212-2035 $12.50

Scheme 1



Reagents and conditions: *a*. $Me_2C{=}CH_2$/Amberlyst H-15, 25 °C, 15 h; *b*. Cu_2Cl_2—NH_2OH—*t*-$BuNH_2$, 10→35 °C, 3 h; *c*. H_2—Ru/C, then Pt/C, 20 °C; *d*. CBr_4—PPh_3/CH_2Cl_2, 0→20°C; *e*. *n*-BuLi—THF—HMPA, −10→−30 °C; *f*. MeOH/TsOH (Cat.), 55 °C, 2 h; *g*. CrO_3—H_2SO_4/Me_2CO, −10 °C; *h*. CF_3COOH, 20 °C, 24 h; *i*. H_2—Ni(P-2)/EtOH, 20 °C; *j*. $(2\text{-}NC_5H_4S)_2$—PPh_3—$AgClO_4$/MeCN, 135—140 °C.

which is used for *C*-alkylation of 3-butyn-1-ol. This step completes the assembly of the entire carbon chain of macrolide **1**. The subsequent necessary transformations of the functional groups give 11-hydroxy-3(*Z*)-dodecenoic acid (**11**), which is a known precursor of ferrulactone II. This route makes it possible to perform all of the reactions with one *tert*-butyl protective group.

"Unsymmetric" diynol **4** was prepared in the presence of cuprous chloride, butylamine, and hydroxylamine hydrochloride.[14] Under these conditions only minor amounts (2—6 %) of symmetric diynes were produced, which could be easily separated by chromatography on Al_2O_3 owing to the difference in polarities.

Exhaustive hydrogenation of compound **4** over Pd- or Pt-catalysts was accompanied by the hydrogenolysis of the C—O bond. However, when 5 % Ru/C and 10 % Pt/C catalysts were used in succession, the side processes were almost suppressed, and ester **5**, which has not been described previously, was obtained in 94 % yield. Substitution of bromine for the primary hydroxyl group in alcohol **5** by the action of CBr_4 in the presence of Ph_3P (*cf.* Ref. 15) gave the key intermediate, C_8 bromide **6**, in 70 % overall yield over four synthetic operations* starting from acetylenic alcohol **2**. The subsequent transformations of bromide **6** involved coupling with lithium 1-(2-tetrahydropyranyloxy)-3-butyn-4-ide to give diether (**7**), which was converted to alkynol **8** by removal of the tetrahydropyranyl protection. It turned out that the oxidation of alcohol **8** by the Jones reagent occurs chemoselectively to afford 11-*tert*-butoxy-3-dodecynoic acid (**9**) in a high yield. Considering the latter reaction, an obvious advantage of the *O-tert*-butyl protection used should be noted; namely, it does not require preliminary reprotection of the OH group (*cf.* Refs. 6—9); this makes it possible to decrease the number of steps in assembling the carbon skeleton of the C_{12} acid and other related acids. The overall yield of acid **9** over seven synthetic steps was 40 %.

The structures of compounds **3—9** prepared for the first time were confirmed by the data from elemental and spectroscopic analyses.

To complete the synthesis of compound **1**, the *O-tert*-butyl protection was removed by trifluoroacetic acid.[17] This afforded the hydroxyynoic acid (**10**), which was then converted to the target lactone **1** by the known pathway: selective *cis*-hydrogenation over a Ni(P-2) catalyst[18] followed by macrolactonization;[6—8] the yield of compound **1** was ~29 % over two steps. The overall yield of ferrulactone II based on the acetylenic alcohol **2** amounted to 9.7 % (over 10 steps).

Experimental

IR spectra were recorded in thin film on a UR-20 (Carl Zeiss) spectrophotometer; UV spectra were obtained with a UV-VIS spectrometer; ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker WM-250 spectrometer (Germany) operating at 250 and 63.89 MHz.

The course of the reaction was monitored by TLC on SiO_2 plates (Silufol). The evaporation of solvents in the isolation of reaction products was carried out on a rotary evaporator at a residual pressure of 15—30 Torr and at a bath temperature of no more than 40 °C. The solvents for the reactions were distilled under argon from an appropriate drying agent (CaH_2,

* According to the literature data, the transition from β-hydroxybutyrate[8] or 2-acetylcyclohexanone[16] to type **6** C_8-halides is usually accomplished in 7—8 synthetic steps.

Na, Na-benzophenone). The starting 3-butyn-1-ol and 4-pentyn-2-ol (**2**) were prepared in 76—80 % yields by treating Li acetylide in liquid NH_3 at −40 °C with ethylene oxide or propylene oxide in DMSO;[19,20] 3-bromo-2-propyn-1-ol (b.p. 62 °C (1 Torr), n_D^{20} 1.5170) was prepared from 2-propyn-1-ol by the hypobromite method with the "reverse" order of addition of the reagents,[19] yield 52 %; 1-(2-tetrahydropyranyloxy)-3-butyne was obtained[21] from 3-butyn-1-ol in the presence of HCl, yield 78 %.

2-*tert*-Butoxy-4-pentyne (3). 150 mL of isobutylene and 10.5 g of Amberlyst H-15 resin* (as the catalyst) were added to a solution of alcohol **2** (42 g, 0.5 mol) in 70 mL of hexane, with cooling to 5 °C. The mixture was stirred for 18—20 h in an autoclave at ~25 °C. The cation-exchanger was filtered off, and the organic layer was washed with water and distilled from $NaHCO_3$. The yield of **3** was 61.5 g (95 %), b.p. 83—84 °C (130 Torr), n_D^{20} 1.4207. IR, ν/cm^{-1}: 3300 and 2110 (C≡CH); 1190 (C—O). ^{1}H NMR, δ: 1.06 (d, J = 6.5 Hz, 3 H, CH_3); 1.15 (c, 9 H, $C(CH_3)_3$); 1.96 (t, J = 2 Hz, 1 H, ≡CH); 2.23 (dd, J = 6.5 Hz and 2 Hz, 2 H, CH_2C≡); 3.72 (sextet, J = 6.5 Hz, 1 H, CH—O). ^{13}C NMR, δ: 81.7 and 73.5 (C≡CH); 69.6 (—C—O); 68.1 (HC—O); 28.4 (CH_2C≡); 22.2 (CH_3). Found (%): C, 77.16; H, 11.42. $C_9H_{16}O$. Calculated (%): C, 77.09; H, 11.50.

7-*tert*-Butoxy-2,4-octadiyn-1-ol (4). A solution of 3-bromo-2-propyn-1-ol in 50 mL of methanol was added dropwise with stirring in an atmosphere of argon over 2 h to a mixture of alkyne **3** (0.11 mol), Cu_2Cl_2 (0.22 g), 40 % aqueous *tert*-butylamine (0.2 mol), and $NH_2OH \cdot HCl$ (0.22 g) in 200 mL of methanol at ~10 °C (water bath). The temperature of the mixture slowly increased to 34 °C. The blue coloration characteristic of Cu^{II} that appeared at the end of the reaction was removed by the periodic addition of additional portions of $NH_2OH \cdot HCl$ (0.1 g). The mixture was kept for 2 h at 40 °C, concentrated, diluted with an equal volume of 0.1 *N* HCl, and thoroughly extracted with ether. The extract was washed with saturated brine and dried with $MgSO_4$. The product was purified by flash-chromatography on Al_2O_3 using a hexane—Et_2O mixture (0→40 % Et_2O) as the eluent. Yield 17.1 g (88 %), b.p. 98—101 °C (0.2 Torr), n_D^{20} 1.5076. IR/ν, cm^{-1}: 3420 (OH); 2260 (C≡C); 1390, 1260, 1200, 1124, 1092, 1040, 1002, 988. UV (heptane), λ_{max}/nm (ε): 214 (460), 226 (410), 241 (430), 253 (270). ^{1}H NMR, δ: 1.18 (s, 9 H); 1.20 (d, J = 6 Hz, 3 H, CH_3); 2.36 (m, 2 H, CH_2C≡); 2.80 (br.s, OH); 3.76 (m, 1 H, CH—O); 4.28 (br.s, 2 H, CH_2O). ^{13}C MNR, δ: 78.5, 74.2, and 65.8 (—C≡CC≡C—); 70.2 (C—O); 66.3 (CH—O); 50.8 (CH_2—O); 29.1 (CH_2C≡). Found (%): C, 73.96; H, 9.17. $C_{12}H_{18}O_2$. Calculated (%): C, 74.19; H, 9.34.

7-*tert*-Butoxyoctan-1-ol (5). A suspension of diynone **4** (5.82 g, 0.03 mol) in 120 mL of alcohol containing 140 mg of 5 % Ru/C** was hydrogenated at ~20 °C under H_2 pressure of 1 atm. When ~1.9 moles of H_2 was absorbed (2.5 h), the reduction slowed down. The Ru catalyst was filtered off, 150 mg of 10 % Pd/C was added to the catalyzate, and the hydrogenation was continued to saturation (4 h, according to TLC). The catalyst was filtered off, and the product was distilled from $NaHCO_3$ to give 5.7 g (94 %) of compound **5**, b.p. 90—92 °C (0.3 Torr), n_D^{20} 1.4426. ^{1}H NMR, δ: 1.06 (d, J = 6.5 Hz, 3 H, $-CH_3$); 1.13 (s, 9 H, $(CH_3)_3C$); 1.1—1.8 (m, 10 H, CH_2); 3.2—3.7 (m, 3 H, CH—O and CH_2—O); no signals were observed in the C=C-region. ^{13}C NMR, δ: 72.1 (C—O); 67.2 (CH—O); 61.8 (CH_2O). Found (%): C, 71.04; H, 12.68. $C_{12}H_{26}O_2$. Calculated (%): C, 71.23; H, 12.95.

1-Bromo-7-*tert*-butoxyoctane (6). A solution of CBr_4 (8.3 g, 25 mmol) in 30 mL of CH_2Cl_2 was added dropwise over 1.5 h to a solution of alcohol **5** (4.35 g, 21 mmol) and triphenylphosphine (7.85 g, 30 mmol) in 30 mL of dry CH_2Cl_2 at 0—4 °C under Ar. The reaction mixture was kept for 4 h at 25 °C, diluted with a hexane—ether mixture (1 : 1, 100 mL), and filtered through a pad of silica gel. The precipitate was washed with ether, the filtrate was concentrated, and the residue was chromatographed on a column with 10 g of SiO_2 and distilled from CaH_2. The yield was 5.0 g (90 %), b.p. 100 °C (1.5 Torr), n_D^{20} 1.4607. IR, ν/cm^{-1}: 1190 (C—O). ^{1}H NMR, δ: 1.06 (d, J = 6.5 Hz, 3 H, CH_3); 1.13 (s, 9 H, $(CH_3)_3C$); 1.18—1.46 (m, 8 H, CH_2); 1.81 (quint, J = 7 Hz, 2 H, CH_2CH_2Br); 3.36 (t, J = 7 Hz, 2 H, CH_2Br); 3.42 (sextet, J = 7 Hz, 1 H, CH—O). ^{13}C NMR, δ: 72.8 (C—O); 67.0 (CH—O); 38.7 (CH_2Br).

11-*tert*-Butoxy-3-dodecyn-1-ol (8). 18 mmol of BuLi in 9 mL of hexane was added dropwise to a solution of 1-(2-tetrahydropyranyloxy)-3-butyne (2.8 g, 18 mmol) in 25 mL of THF stirred under Ar at −5 °C. The mixture was kept for 2 h at ~0 °C, then a solution of freshly distilled bromide **6** (2.65 g, 10 mmol) in 12 mL of HMPT was added at −15÷−12 °C over 1 h, and after 1 h the mixture was heated to ~20 °C over 10 min. After 18 h (25 °C) the mixture was gently heated (28—30 °C) for 4 h, decomposed with water, and extracted with ether (3×30 mL). The resulting tetrahydropyranyl ether **7** (the residue, 4.2 g) was solvolyzed without purification by refluxing for 2 h in 40 mL of MeOH in the presence of 0.2 g of TsOH, then concentrated, diluted with ether, and neutralized with $NaHCO_3$. The usual workup of the organic layer gave 2.6 g of a compound, which was chromatographed on SiO_2. Elution with a hexane—ether (2 : 1) mixture gave 1.9 g (75 %) of acetylenic alcohol **8** as a homogeneous oil (according to TLC), n_D^{20} 1.4638. IR, ν/cm^{-1}: 3450, 1190, 1050. ^{1}H NMR, δ: 1.08 (d, J = 6.5 Hz, 3 H, CH_3); 1.16 (s, 9 H); 1.20—1.52 (m, 10 H, CH_2); 2.13 and 2.40 (both m, 4 H, CH_2C≡); 3.54 (sextet, J = 6.5 Hz, 1 H, CH—O); 3.65 (t, J = 6.5 Hz, 2 H, CH_2O). ^{13}C NMR, δ: 82.0 and 76.4 (C≡C); 73.0 (C—O); 67.3 (CH—O); 61.1 (CH_2O). Found (%): C, 75.30; H, 11.57. $C_{16}H_{30}O_2$. Calculated (%): C, 75.53; H, 11.89.

11-*tert*-Butoxy-3-dodecynoic acid (9). 2.5 mL of an 8 *N* solution of the Jones reagent was added dropwise to a vigorously stirred solution of alcohol **8** (0.76 g, 3 mmol) in 12 mL of acetone under Ar at ~−10 °C, the mixture was kept for 0.5 h at ~0 °C, and at ~−10 °C an additional 2 mL of this reagent was added dropwise. The mixture was kept at ~0 °C until compound **8** disappeared (1.5 h, according to TLC). The excess of the reagent was quenched at ~0 °C by the addition of 3 mL of 2-propanol, and the mixture was diluted with water and ethyl acetate. The organic layer was separated, washed with brine, and extracted with 1 *N* NaOH (3 × 4 mL). The aqueous extracts were acidified at 0 °C with 2 *N* HCl, and extracted with a benzene—ethyl acetate mixture (1 : 1). The solvent was evaporated, and the residue was subjected to flash chromatography on SiO_2 (using a 70 : 30 : 1 hexane—ethyl acetate—HCOOH mixture as the eluent). The yield of acid **9** was 0.6 g (76 %). IR, ν/cm^{-1}: 3400—2500, 2220 w, 1720, 1200, 1160, 1120 (no admixture of the allene isomer). ^{1}H NMR, δ: 1.07 (d, J = 6 Hz, 3 H, CH_3); 1.17 (s, 9 H);

* Amberlyst H-15 is a product of Fluka; when H_2SO_4 or KU-2(H^+) resin were used as catalysts, the yield of ether **3** was 83—87 %.

** Kindly provided by E. F. Litvin (N. D. Zelinsky Institute of Organic Chemistry, RAS).

1.1—1.6 (m, 10 H, CH_2); 2.14 (br.t, J = 6.5 Hz, 2 H, $CH_2C{\equiv}$); 3.21 (t, J = 2.2 Hz, 2 H, $\equiv CCH_2CO$); 3.53 (sextet, J = 6.5 Hz, 1 H, CH—O); 9.7 (br.s, COOH). ^{13}C NMR, δ: 174.3 (COOH); 84.4 and 73.7 (C≡C); 71.0 (C—O); 67.8 (CH—O).

11-Hydroxy-3-dodecynoic acid (10). A solution of *tert*-butoxy derivative **9** (0.54 g, 2 mmol) in 10 mL of CF_3COOH was kept for 24 h at 20 °C and carefully evaporated *in vacuo*. The residue was dissolved in ether, the solution was washed with saturated brine and concentrated, and the residue was subjected to flash chromatography on SiO_2 (elution with a 70 : 30 : 1 hexane—ethyl acetate—HCOOH mixture) to give 350 mg of acid **10** as an oil (n_D^{20} 1.4647) containing ~10 % admixture of its allene isomer (according to ^{13}C NMR and IR spectra). IR, ν/cm^{-1}: 3500—3200 (OH); 3500—2500, 1700 br (COOH); 2220 m (C≡C); 1960 (CH=C=CH); 1380, 1280, 1240, 1180, 940. ^{13}C NMR, δ: 213.0, 162.0, and 95.1 (CH=C=CH—); 172.5 (COOH); 83.6 and 81.3 (C≡C); 66.3 (C—O); 61.3 (CH—O). The sample was used for the next step without further purification.

11-Hydroxy-3(*Z*)-dodecenoic acid (11). Crude acid **10** (320 mg, 1.5 mmol) was hydrogenated* over the Ni(P-2) catalyst according to the procedure given in Ref. 18 in the presence of $Ni(OAc)_2 \cdot 2H_2O$ (470 mg), $NaBH_4$ (80 mg), ethylenediamine (0.33 mL), and 12 mL of ethanol; H_2 was quantitatively absorbed over 40 min. The reaction mixture was kept for an additional 0.5 h, filtered, and diluted with ether. The organic layer was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was subjected to flash chromatography on SiO_2 using a 70 : 30 : 1 hexane—ethyl acetate—HCOOH mixture as the eluent to give 290 g (91 %) of acid **11** as a light-colored oil. IR, ν/cm^{-1}: ~3400, ~2650, 1700, 940 m ((*Z*)-CH=CH—). ^1H NMR, δ: 1.14 (d, J = 6 Hz, 3 H, CH_3); 1.1—1.6 (m, 10 H, CH_2); 1.8—2.3 (m, 2 H); 3.08 (d, J = 5.5 Hz, 2 H, $CH_2C{=}O$); 3.5—3.9 (m, 1 H, CH—O); 5.4—5.7 (m, 2 H, —CH=CH—), *cf.* Refs. 7, 8.

(*R/S*)-3(*Z*)-Dodecen-11-olide (ferrulactone II). A solution of the thioester prepared from 300 mg of acid **11** in 15 mL of MeCN, 0.76 g of Ph_3P, and 0.6 g of 2,2′-dipyridyl disulfide (kept for 2 h and diluted with 120 mL of xylene) was added over 5 h through a reflux condenser to a boiling solution of 1.5 g of $AgClO_4$ in 120 mL of toluene under Ar in a high-dilution apparatus. The mixture was refluxed for 6 h, filtered through 230 g of SiO_2, and chromatographed using mixtures of hexane with Et_2O (0→12 % Et_2O) as eluents to isolate 120 mg of a product, which was rechromatographed on 10 g of SiO_2 to afford 88 mg (~32 %) of lactone **1** of ~92 % purity (according to GLC and ^1H NMR spectroscopy). ^1H NMR, δ: 2.24 (d, J = 7 Hz, 3 H, CH_3); 1.2—1.7 (m, 10 H, CH_2); 2.10 and 2.26 (both m, 2 H, $CH_2C{=}$); 3.02 and 3.12 (both dd, AB part of the ABX-system, J_{gem} = 14, J_{AX} = 7 Hz, J_{BX} = 8 Hz, 2 H, $=CCH_2CO$); 5.04 (br.q, J = 7 Hz, 1 H, CH—O); 5.4—5.7 (m, 2 H, —CH=CH—), *cf.* Refs. 7, 8.

* Hydrogenation of the allenic acid (as an admixture) gives the same product[7] as does hydrogenation of alkynoic acid **10**.

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Received November 11, 1993