A benzene solution of the dry residue from the fraction with a retention time of 6.0-8.0 min yielded 157.6 mg of uracil in crystalline form, Found, %: C 42.11, H 4.00; N 23.72; $C_4H_4N_2O_2$. EI mass spectrum, m/z (intensity, % of the maximum): 112 (100), 69 (65), 68 (23), 42 (67), 41 (34), 40 (37), 39 (9), 28 (68). UV spectrum, $\lambda_{max}^{CH_3OH}$, nm: 258 (log ε 4.12).

The dry residue (1.9 g) from the fraction with a retention time of 8.0-12.0 min, which contained (I) and (II) and accompanying substances, was chromatographed on column of silica gel L 40/100 in a gradient MP of benzene—acetone. The eluate obtained with the MP benzene—acetone (55:45) was evaporated to dryness, giving 370 mg of a product in the form of a colorless film. IR spectrum, ν, cm^{-1}: 3379 (O—H), 2918 (C—H), 1676 (C=C—C=O), 1448, 1377, 1169, 850, 754. UV spectrum: $\lambda_{max}^{CH_3OH}$, nm: 221 (log ε 3.67).

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PHEROMONES OF INSECTS AND THEIR ANALOGS.

XXVII. SYNTHESIS OF 10-HYDROXY-4,8-DIMETHYLDECA-4E,8E-DIENOIC ACID AND OF RACEMIC 4,8-DIMETHYLDECANAL FROM GERANYL ACETATE

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10-Hydroxy-4,8-dimethyldeca-4E,8E-dienoic acid and racemic 4,8-dimethyldecanal (components of beetle pheromones) have been synthesized from geranyl acetate.

A number of schemes for the synthesis of 10-hydroxy-4,8-dimethyldeca-4E,8E-dienoic acid (I) [1-4] and of racemic 4,8-dimethyldecanal (II) [5-10] have been published. The first of these compounds is an acyclic precursor of the aggregation component of the pheromone of the grain beetle *Cryptolests ferrugineus* [1, 2], and the second exhibits a high activity [5] in relation to the flour beetles *Tribolium castaneum* and *T. confusum*, the aggregation pheromone of which is, according to the literature [11-13], a mixture of the optically active 4R,8R and 4R,8S diastereomers of the aldehyde (II). We have developed a scheme for the synthesis of compounds (I) and (II) that starts from geranyl acetate (III). The latter was converted into 8-acetoxy-2,6-dimethylocta-2E,6E-dien-1-ol (IV) and then into the corresponding chloride (V) according to [3, 14]. The interaction of the chloride (V), as of the corresponding bromide [3] with sodiomalonic ester led to the coupling product (VI) with a yield of 76%. We have

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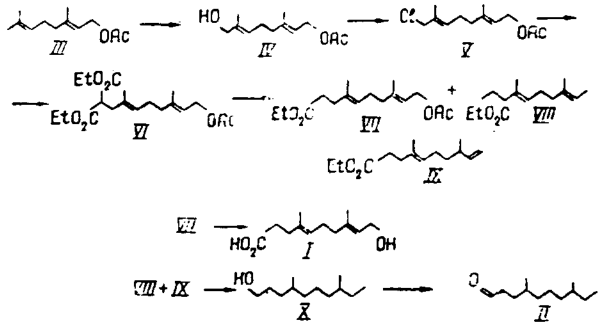
found that the yield of malonic ester derivative (VI) rises to 90% when this reaction is catalyzed with the aid of the complex $Pd(OAc)_2 \cdot PPh_3$, the reaction taking place rapidly and requiring no heating. The decarboxylation of the geminal diester (VI) on heating in aqueous DMFA or DMSO in the presence of LiCl gave the expected product (VII) with yields of 58 and 26%, respectively. In addition to compound (VII) the product of its hydrogenolysis at the acetoxy group, consisting of a mixture of esters of the regioisomeric 4,8-dimethyldeca-8,9- and -9,10-dienoic acids (VIII and IX, respectively), was obtained. The yields of (VIII) and (IX) were high when the reaction was performed in DMSO, while when the time of the reaction was more than 30 min the hydrogenolysis product was obtained exclusively and the yield of the mixture of esters (VIII) and (IX) amounted to 71%.

The presence of compound (IX) with double bonds shifted into the terminal position in the hydrogenolysis product was confirmed by the appearance in the IR spectrum of absorption bands characteristic for a terminal vinyl group in the 920 and 1000 cm^{-1} regions, in the ^{13}NMR sspectrum* of signals at 113.07 and 144.96 ppm and in the ^{1}H NMR spectrum of two multiplets of a three-spin system in the 5.2-5.5 and 6.3-6.5 ppm regions [15]. The ratio of the intensities of the signals of carbon atoms of the Δ^8 double bond in (VIII) (138.93 and 115.78 ppm) and of the Δ^9 double bond in (IX) (145.96 and 113.03 ppm) indicated the predominance of compound (VIII) in the mixture. It followed from the results of GLC analysis that compounds (VII) and (IX) were present in the hydrogenolysis product in a ratio of 7:3. The production of the decarboxylation of (VII) was readily separated from the mixture of (VIII) and (IX) with the aid of column chromatography, and after alkaline hydrolysis it gave one of the desired compounds (the hydroxy acid (I)) in an overall yield of 14.5%, calculated on the initial (III).



The hydrogenation of the mixture of compounds (VIII) and (IX) over a palladium catalyst and subsequent treatment with $i-Bu_2AlH$ gave the saturated alcohol (X), the oxidation of which with pyridiunium chlorochromate led to the pheromone (II) with an overall yield of 15.5%, calculated on the initial (III).

EXPERIMENTAL

IR spectra were taken on a Ur-20 spectrometer (in a film), and PMR spectra were recorded on a Tesla BS-567 instrument (working frequency 100 MHz, solvent $CDCl_3$), or, for compound (V), a Tesla BS-467 instrument (60 MHz, CCl_4). ^{13}C NMR spectra were taken on a Jeol FX-90Q spectrometer (22.5 MHz) with broad-band and off-resonance suppression for protons, the solvent being $CDCl_3$. Chemical shifts are given in the δ scale relative to the signal of TMS (internal standard). GLC was conducted on a Chrom-5 instrument with, as stationary phase, the silicone liquid SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.2 mm) at a working temperature of 50-300°C, the carrier gas being helium.

8-Chloro-3,7-dimethylccata-2E,6E-dien-1-yl Acetate (V). At −15°C, phosgene was passed at the rate of 2 liters/h for 0.5 h into a mixture of 0.38 g of absoute DMFA, 2.04 ml of absolute pyridine, and 17.4 ml of absolute CH_2Cl_2 was added dropwise to the resulting bright red suspension. The temperature of the reaction mixture was raised to 0°C and it was stirred for 1.5 h, after which it was diluted with 200 ml of diethyl ether, and 30 ml of a 20% solution of AcONa was added. The organic layer was separated off, washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. The residue was chromatographed (SiO_2, hexane–diethyl ether (1:1)). This gave 2.76 g (85%) of (V), R_f 0.60, n_D^{28} 1.4740 [16]. IR spectrum (ν, cm^{-1}): 700 (C−Cl) 865(C=C−H), 1245 (C−O−C), 1375, 1390 (CH_3), 1670 (C=C), 1740 (C=O). PMR spectrum

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*The values of δ in the ^{13}C NMR spectra of compounds (VIII) and (IX) coincide for the C^1–C^6 fragment but differ for the C^7–C^{10} fragment.

(δ, ppm): 1.65 (br.s, 6H, CH_3-3, CH_3-7), 1.89 (s, 3H, CH_3CO), 1.95-2.25 (m, 4H, H-4, H-5), 3.85 (s, 2H, H-8), 4.39 (d, 2H, J = 7 Hz, H-1), 5.0-5.5 (m, 2H, H-2, H-6).

Ethyl 10-Acetoxy-2-ethoxycarbonyl-4,8-dimethyldeca-4E,8E-dienoate (VI). a) With stirring (Ar, 16°C) a solution of sodiomalonic ester obtained from 1.4 g (8 mmole) of ethyl malonate and 0.18 g (8 mg-atom) of sodium in 20 ml of absolute THF (Ar, 20°C) was added over 0.5 h to a solution of 9 mg (0.04 mmole) of $Pd(OAc)_2$, 42 mg (0.16 mmole) of triphenylphosphine, and 0.46 g (2 mmole) of the chloride (V) in 2 ml of absolute THF. After 0.3 h, the reaction mixture was cooled to −10°C, 3 ml of 1 M H_2SO_4 was added, and it was extracted with diethyl ether (3 × 100 ml). The combined extracts were washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. The unchanged diethyl malonate was distilled off at 92°C (18 mm), and the still residue was chromatographed (SiO_2, hexane—diethyl ether (1:1)).

This gave 0.65 g (92%) of compound (VI), n_D^{24} 1.4630, R_f 0.39. Its PMR spectrum was identical with that describe in the literature [3]. IR spectrum (ν, cm^{-1}): 870 (C=C—H), 1245 (C—O—C), 1380 (CH_3), 1670 (C=C), 1745 (C=O). ^{13}C NMR spectrum (δ, ppm): 14.14 (q, $\underline{C}H_3CH_2O$), 61.33 (t, $CH_3\underline{C}H_2O$), 169.20 (s, C_1, EtO_2C-2), 50.82 (d, C_2), 38.52 (t, C_3), 131.34 (s, C_4), 14.58 (q, CH_3-4), 126.68 (d, C_5), 26.22 (t, C_6), 39.23 (t, C_7), 141.95 (s, C_8), 15.77 (q, CH_3-8), 118.44 (d, C_9), 61.17 (t, C_{10}), 21.08 (q), 172.63 (s, O=C—O-10), 21.08 (q, $\underline{C}H_3CO$).

b) A solution of sodiomalonic ester, obtained from 0.114 g (6 mmole) of sodium hydride and 0.96 g (6 mmole) of ethyl malonate in 18 ml of absolute DMFA (Ar, 20°C) over 0.5 h, was treated with 1.15 g (5 mmole) of the chloride (V) and the mixture was stirred at 60°C for 4.5 h and at 23°C for 12 h, after which 25 ml of water was added and the whole was extracted with diethyl ether (3 × 150 ml). The extract was worked up as described above. This gave 1.35 g (76%) of compound (VI), identical with the compound obtained in the preceding experiment.

Ethyl 10-Acetoxy-4,8-dimethyldeca-4E,8E-dienoate (VII) and a Mixture of Ethyl 4,8-Dimethyldeca-4E,8E- and -4E,9-dienoates (VIII) and (IX). a) A solution of 0.65 g (1.84 mmole) of (VI) in 4.2 ml of DMSO was treated with 0.31 g (7.3 mmole) of LiCl and 66.3 mg (3.6 mmole) of water and the mixture was heated at 173°C until the triester (VI) had undergone complete conversion (0.3 h, monitoring by TLC); then 10 g of ice was added and the whole was extracted with n-hexane (3 × 50 ml). The combined extracts were washed with water (5 ml) and with saturated NaCl solution (10 ml) and were dried with $MgSO_4$ and evaproated. The residue was chromatographed (SiO_2, hexane—diethyl ether (1:1)). This gave 0.14 g (26%) of compound (VII) (R_f 0.50, n_D^{24} 1.4640); PMR spectrum identical with that described in [3]; and 0.19 g (47%) of a mixtue (7:3 according to GLC) of the esters (VIII) and (IX) (R_f 0.74).

For compound (VII): IR spectrum (ν, cm^{-1}): (C=C—H), 1248 (C—O—C), 1380, 1390 (CH_3), 1672 (C=C), 1740 (C=C); ^{13}C NMR spectrum (δ, ppm): 14.25(q), 61.28 (t), (OEt), 173.32 (s, C_1), 34.62 (t, C_2), 33.21 (t, C_3), 133.83 (s, C_4), 16.42 (q, CH_3-4), 124.40 (d, C_5), 26.06 (t, C_6), 39.34 (t, C_7), 141.90 (s, C_8), 15.93 (q, CH_3-8), 118.44 (d, C_9), 60.20 (t, C_{10}), 21.02 (q), 171.00 (s) (OAc).

For the mixture of (VIII) and (IX): ^{13}C NMR spectrum (δ, ppm): 14.25 (q), 60.52 (t) (OEt), 173.48 (s, C_1), 34.68 (t, C_2), 33.27 (t, C_3), 133.77 (s, C_4), 15.98 (q, CH_3-4), 124.83 (d, C_5), 26.55 (t, C_6), 31.26 (t, $^{VIII}C_7$), 37.98 (t, $^{IX}C_7$), 138.93 (s, $^{VIII}C_8$), 35.06 (d, $^{IX}C_8$), 2.65(q, ^{VIII} CH_3-8), 22.16 (q, ^{IX}CH-8), 115.78(d, $^{VIII}C_9$), 145.96(d, $^{IX}C_9$), 13.94(q, $^{VIII}(C_{10})$, 113.03 (t, $^{IX}C_{10}$).

b) A solution of 0.65 g (1.84 mmole) of (VI) in 4.3 ml of DMFA was treated with 0.31 g (7.3 mmole) of LiCl and 68 mg (3.79 mmole) of water and the mixture was heated at 173°C until compound (VI) had undergone complete conversion (0.5 h, monitoring by TLC). Then the product was worked up as described in the preceding experiment. This gave 0.3 g (58%) of compound (VII) and 0.052 g (13%) of a mixture (7:3) of the esters (VIII) and (IX).

c) A solution of 0.65 g (1.84 mmole) of (VI) in 4.2 ml of DMSO was treated with 0.294 g (6.93 mmole) of LiCl and 65 mg (3.57 mmole) of water and the mixture was heated at 173°C until compounds (VI) and (VII) had undergone complete conversion (1 h, monitoring by TLC). The product was then worked up as described in experiment a). This gave 0.29 g (71%) of a mixture (7:3) of the esters (VII) and (IX). The characteristics of the compounds (VII-IX) obtained in experiments b) and c) were identical with those given for experiment a).

10-Hydroxy-4,8-dimethyldeca-4E,8E-dienoic Acid (I). A solution of 0.42 g (1.5 mmole) of the diester (VII) in 8 ml of MeOH was stirred at 25°C, and 2.4 ml of a 25% solution of KOH

(15 mmole) was added. The mixture was kept for 5 h and was evaporated and the resiude was acidified with 10% HCl to pH $\leq$ 3 and was extracted with diethyl ether. The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated in vacuum, and the residue was chromatographed on SiO_2. Gradient elution from n-hexane to a 1:1 mixture of it with diethyl ether gave 0.23 g (71%) of the hydroxy acid (I), the IR and PMR spectra of which were identical with those described in the literature [2, 3].

4,8-Dimethyldecan-1-ol (X). A mixture of 0.23 g (1 mmole) of the mixed esters (VIII) and (IX), 10 ml of absolute ethanol, and 0.05 g of 5% Pd/C was stirred in an atmosphere of hydrogen until the absorption of hydrogen had ceased (40 h), and it was then filtered. and evaporated. The residue was dissolved in 5 ml of absolute diethyl ether and, at −15°C under Ar, 0.64 ml (2.8 mmole) of a 73% solution of DIBAH in toluene was added and the resulting mixture was stirred at −10°C for 1.5 h, after which 1 ml of water was added at 0-5°C and stirring was continued at 20°C for 2 h and extraction with diethyl ether (3 × 50 ml) was carried out. The combined extracts were washed with saturated NaCl solution, dried with Na_2SO_4, and evaporated. This gave 0.17 g (1%) of the alcohol (X), n_D^{26} 1.4378; IR and PMR spectra identical with those described in the literature [17].

4,8-Dimethyldecanal (II). A solution of 0.1 g (0.54 mmole) of the alcohol (X) in 0.5 ml of CH_2Cl_2 was added to a stirred suspension of 0.18 g (0.8 mmole) of pyridinium chlorochromate in 1 ml of absolute Ch_2Cl_2, the mixture was stirred at room temperature for 1 h, and then it was diluted with 5 ml of diethyl ether and was filtered through a layer of SiO_2. The residue on the filter was washed with 50 ml of diethyl ether, and the solution was dried with $MgSO_4$ and evaporated. The residue was chromatographed (SiO_2, hexane– diethyl ether (8:2)) to give 0.07 g (68%) of the aldehyde (II) the IR and PMR spectra of which were identical with those described in the literature [9].

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