INSECT PHERMONES AND THEIR ANALOGUES

XXXIX. SYNTHESIS OF 11RS-HYDROXY- AND 12-HYDROXYDODEC-3Z-ENOIC ACIDS – ACYCLIC PRECURSORS OF THE MACROLIDE COMPONENTS OF THE PHEROMONES OF Cryptolestes ferrugineus and C. pusillus

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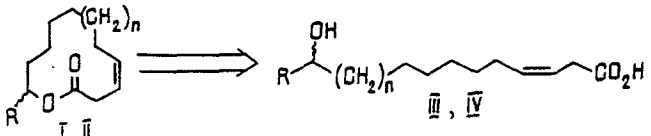
A new approach to the synthesis of 11RS-hydroxy- and 12-hydroxydodec-3Z-enoic acids has been developed with the use, in one of the key stages, of the partial ozonolysis of the acetates of the corresponding methylene-separated enynic alcohols.

The macrolide components of the aggregation pheromones of the rust-red grain beetle (Cryptolestes ferrugineus) [1-3] and the flat grain beetle (C. pusillus) [4], which have the structures of dodecen-11- and -12-olides [(I) and (II), respectively], have been obtained by the cyclization of 11RS-hydroxy- and 12-hydroxydodec-3Z-enoic acids [(III) and (IV), respectively) [5, 6].

The hydroxy acids (III) and (IV) have previously been obtained from ω-hydroxy derivatives of allenecarboxylic acids [4] or from alk-3-yn-1-ols [5].

We have discovered a new approach to the synthesis of these compounds with the use, in one of the key stages, of the selective ozonolysis of acetates of aliphatic alcohols with a 1,4-enynic fragment at the end of the chain. The starting compounds in this process were the readily accessible [7-9] tetrahydropyranyl ethers of terminal alkyn-1-ols (V-VII) the conversion of which into the required methylene–separated alkenynes was begun by their coupling with allyl bromide. The further transformations of the resulting undec-10-en-7-yn-1-ol (VIII), dodec-11-en-8-yn-1-ol (IX), and tridec-12-en-9-yn-1-ol (X), obtained in high yields, were as follows. The bromination of alcohol (VIII) with the $Br_2P{\cdot}Ph_3$ complex gave with a yield of 83% the corresponding bromide (XI), the generation of the Grignard reagent from which and its subsequent treatment first with acetaldehyde and then with acetic anhydride led with satisfactory yield to the tridec-12-en-9-yn-2RS-yl acetate (XIII). The yield of the latter increased more than twofold on the use for its synthesis of a different route including the stage of oxidizing the alcohol (IX) and condensing the resulting aldehyde (XII) with methylmagnesium iodide, followed by treatment with acetic anhydride.



I, II — III, IV

R = Me (I, III), H (II, IV); n = 1 (I, III), 2 (II, IV).

The partial ozonolysis of the enyne acetate (XIII) took place exclusively at the double bond and, after the oxidation of the peroxide peroxide with the Jones reagent, gave 11RS-acetoxydodec-3-ynoic acid (XIV). Alkaline hydrolysis of the acetate (XIV) followed by catalytic hydrogenation of the hydroxyalkynoic acid (XV) obtained concluded the synthesis of one of the desired compounds – the racemic (Z)-hydroxyalkenoic acid (III), its overall yield, calculated on the initial alkynol (VI) being 27%.

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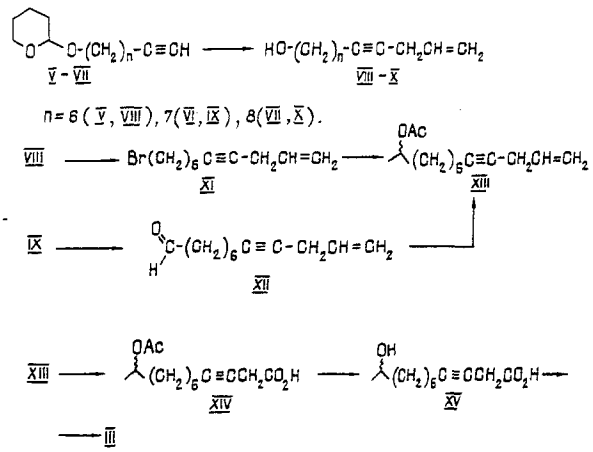
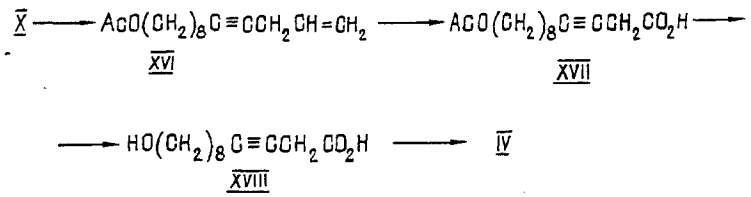


The second desired product – the (Z)-hydroxyalkenoic acid (IV) – was synthesized by analogous transformations but via a smaller number of stages and in far higher overall yield (60%) from the enynic alcohol (X) through the intermediate compounds (XVI-XVIII).



EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in films), and PMR spectra were recorded on a Tesla BS-567 instrument (working frequency 100 MHz) with $CDCl_3$ as solvent, the chemical shifts being given on the δ scale relative to the signal of TMS (internal standard). TLC analysis was conducted on a Chrom-5 instrument with, as the stationary phase, silicone liquid SE-30 (5%) on Chromaton N-AW-DMCS (0.16-0.20 mm) at working temperatures of 50-300°C, with helium as the carrier gs. TLC was performed on Silufol-brand plates weith a fixed layer of silica gel. The analyses of the compounds synthesized corresponded to the calculated figures.

Undec-10-en-7-yn-1-ol (VIII). A solution of 31.5 g (0.15 mole) of 1-(tetrahydropyran-2-yloxy)oct-7-yne [7] in 30 ml of absolute THF was added after 30 minutes to a stirred (20°C, Ar) suspension 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 absolute 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 to it. 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 and the residue was dissolved in 340 ml of methanol containing 6.8 g of TsOH, and this mixture was stirred at room temperature for 24 h, concentrated in vacuum, diluted with diethyl ether, washed successively with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated.

The residue was distilled, to give 20.9 g (84%) of the alcohol (VIII), bp 120-121°C (4 mm) n_D^{23} 1.4957. IR spectrum (ν, cm^{-1}): 920, 1000, 1650 and 3090 (CH=CH_2), 2230 (C≡C), 1065 (C–O), 3350 (OH). PMR spectrum (100 MHz, $CDCl_3$): 1.45-1.7 (m, 8H, CH_2), 2.2 (m, 2H, H-6), 2.88-3.0 (m, 2H, H-9), 3.65 (t, 2H, J=7 Hz, H-1), 5.05-5.4 (m, 2H, H-11), 5.65-6.1 (m, 1H, H-10).

Dodec-11-en-8-yn-1-ol (IX). A solution of 33.6 g (0.15 mole) of 1-(tetrahydropyran-2-yloxy)non-8-yne (VI) [8] in 30 ml absolute THF was added after 20 minutes to a stirred (20°C, Ar) suspension 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 absolute diethyl ether, and the reaction mixture was then worked up as described from compound (VIII). This gave 23.5 g (87%) of the alcohol (IX),

bp 56-58°C (1 mm), n_D^{23} 1.4970. IR spectrum (ν, cm^{-1}): 920, 990, 1645 and 3085 (CH=CH_2), 2230 (C≡C), 1065 (C–O), 3350 (OH). PMR spectrum (100 MHz, $CDCl_3$): 1.4-1.7 (m, 10H, CH_2), 2.2 (m, 2H, H-7), 2.9-3.0 (m, 2H, H-10), 3.64 (t, 2H, J = 7 Hz, H-1), 5.0-5.4 (m, 2H, H-12), 5.65-6.0 (m, 1H, H-11).

Tridec-12-en-9-yn-1-ol (X). A solution of 35.7 g (0.15 mole) of 1-(tetrahydropyran-2-yloxy)dec-9-yne (VII) [9] in 40 ml of absolute THF was added after 20 min to a stirred (20°C, Ar) suspension 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 absolute diethyl ether, and the reaction mixture was then worked up as described for compound (VIII). This gave 24.7 g (85%) of the alcohol (X), bp 143-145°C (4.5 mm), n_D^{23} 1.4992. IR spectrum (ν, cm^{-1}): 920, 990, 1645 and 3085 (CH=CH_2), 2225 (C≡C), 1060 (C–O), 3350 (OH). PMR spectrum (100 MHz, $CDCl_3$): 1.4-1.7 (m, 12H, CH_2), 2.2 (m, 2H, H-8), 2.9-3.0 (m, 2H, H-11), 3.64 (t, 2H, J = 7 Hz, H-1), 5.0-5.4 (m, 2H, H-13), 5.6-6.1 (m, 1H, H-12).

1-Bromodec-10-en-7-yne (XI). 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 and, after 0.5 h 13.4 g ($80.8 \cdot 10^{-3}$ mole) of the alcohol (VIII) was added. After 3 h the mixture was diluted with pentane, filtered through a layer of SiO_2 (150 g) and evaporated in vacuum. This gave 15.4 g (83%) of the bromide (XI), n_D^{23} 1.5092. IR spectrum (ν, cm^{-1}): 570, 655 (C–Br), 920, 990, 1645 and 3085 (CH=CH_2), 2220 (C≡C). PMR spectrum (100 MHz, $CDCl_3$): 1.45-1.9 (m, 8H, CH_2), 2.2 (m, 2H, H-7), 2.87-3.0 (m, 2H, H-9), 3.42 (t, 2H, J = 6.5 Hz, H-1), 5.05-5.4 (m, 2H, H-11), 5.65-6.05 (m, 1H, H-10).

Dodec-11-en-8-ynal (XII). A solution of 4.2 g ($23.3 \cdot 10^{-3}$ mole) of the alcohol (IX) in 4 ml of CH_2Cl_2 was added at room temperature to a suspension of 8.6 g ($39.9 \cdot 10^{-3}$ mole) of pyridinium chlorochromate in 46 ml of anhydrous CH_2Cl_2, the mixture was stirred for 2 h and was then diluted with 50 ml of diethyl ether, and the liquid phase was decanted off and was filtered through a layer of SiO_2 (10 g) and evaporated. This gave 3.7 g (89%) of the aldehyde (XII). IR spectrum (ν, cm^{-1}): 920, 990, 1640 and 3085 (CH=CH_2), 2220 (C≡C), 1720 and 2730 (CHO). PMR spectrum (100 MHz, $CDCl_3$): 1.1-1.8 (m, 8H, CH_2), 2.2 (m, 2H, H-7), 2.35-2.58 (m, 2H, H-2), 2.85-3.04 (m, 2H, H-10), 5.0-5.45 (m, 2H, H-12), 5.65-6.08 (m, 1H, H-11), 9.76 (t, 1H, J = 1.8 Hz, H-1).

2RS-Acetoxytridec-12-en-9-yne (XIII). With vigorous stirring, 2 g ($46 \cdot 10^{-3}$ mole) of acetaldehyde in 5 ml of absolute THF was added (0°C, Ar) to a solution of the Grignard reagent obtained at 45-50°c from 0.82 g ($34 \cdot 10^{-3}$ g-atom) of magnesium and 7.73 g ($34 \cdot 10^{-3}$ mole) of the bromide (XI) in 30 ml of absolute THF, and then the mixture was warmed to room temperature and kept for 0.5 h, after which it was again cooled to 0°C and was treated with 6.94 g ($68 \cdot 10^{-3}$ mole) of Ac_2O and again warmed to room temperature; it was stirred for 1 h, treated with 50 ml of saturated NH_4Cl solution, stirred for another 1 h, and extracted with diethyl ether (3 × 100 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 (9:1)), to give 2.5 g (31%) of compound (XIII), n_D^{20} 1.4645. IR spectrum (ν, cm^{-1}): 920, 990, 1645 and 3085 (CH=CH_2), 1240 and 1740 (OAc), 2220 (C≡C). PMR spectrum (100 MHz, $CDCl_3$): 1.20 (d, 3H, J = 6.3 Hz, H-1), 1.3-1.7 (m, 10H, CH_2), 2.02 (s, 3H, CH_3CO), 2.2 (m, 2H, H-8), 2.9-3.0 (m, 2H, H-11), 4.9 (m, 1H, H-2), 5.0-5.4 (m, 2H, H-13), 5.7-6.0 (m, 1H, H-12).

b) A solution of the Grignard reagent obtained from 1.27 g ($9.0 \cdot 10^{-3}$ mole) of CH_3I and 0.22 g ($9.0 \cdot 10^{-3}$ g-atom) of magnesium in 20 ml of absolute diethyl ether was added (0°C, Ar) to a solution of 1.49 g ($8.4 \cdot 10^{-3}$ mole) of the aldehyde (XII) in 20 ml of absolute THF, and the mixture was stirred at 0°C for 0.5 h and at 25°C for 0.5 h; then it was cooled to 0°C, treated with 192 g ($18.9 \cdot 10^{-3}$ mole) of Ac_2O, heated to 25°C and stirred for 0.5 h, after which it was again cooled to 0°C, 10 ml of saturated NH_4Cl solution was added, and the mixture was stirred for 1 h and was extracted with diethyl ether (3 × 50 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 (9:1), to give 1.19 g (60%) of the acetate (XIII), identical with that obtained in the preceding experiment.

11RS-Acetoxydodec-3-ynoic Acid (XIV). At 5°C, an ozone–oxygen mixture (5.5 wt. % of O_3) was passed at the rate of 30 liters/h through a solution of 2.36 g ($10 \cdot 10^{-3}$ mole) of compound (XIII) in 35 ml of cyclohexane and 3.5 ml of AcOH 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, and 1.4 ml ($11.2 \cdot 10^{-3}$ mole) of a 8 N solution

of H_2CrO_4 was added; the resulting mixture was stirred for 0.5 h and was then heated to 20°C and stirred for another 4 h, after which 1 ml of isopropanol was added (to decompose the excess of oxidant) and it was evaporated in vacuum. The residue was dissolved in water and extracted with diethyl ether (3 × 50 ml).

By the action of a saturated solution of $NaHCO_3$, a salt of the acid (XIV) was extracted from the organic layer into the aqueous layer, and this was acidified with 10% HCl to pH ≤ 3 and was extracted with diethyl ether (3 × 100 ml). The extract was washed with saturated NaCl solution, dried with Na_2SO_4, and evaporated. This gave 1.7 g (67%) of the acetoxy acid (XIV) in the form of a colorless oil, R_f 0.45 (hexane–diethyl ether (1:3)). PMR spectrum (100 MHz, $CDCl_3$): 1.20 (d, 3H, J = 7 Hz, H-12), 1.3-1.7 (m, 10H, CH_2), 2.04 (s, 3H, CH_3CO), 2.2 (m, 2H, H-5), 3.32 (t, 2H, J = 2.5 Hz, H-2), 4.9 (m, 1H, H-11), see [10, 11].

11RS-Hydroxydodec-3-ynoic Acid (XV). A mixture of 0.45 g ($1.77 \cdot 10^{-3}$ mole) of the acetoxy acid (XIV) and 2.4 g (17.40^{-3} mole) of K_2CO_3 in 5 ml of MeOH was heated at 50°C for 2 h and was then acidified with 10% HCl to pH ≤ 3 and extracted with diethyl ether (3 × 50 ml). The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. This gave 0.35 g (94%) of the hydroxy acid (XV) 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 [10, 11].

11RS-Hydroxydodec-3Z-enoic Acid (III). A suspension of 0.31 g ($8.2 \cdot$ $^{-3}$ 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 over 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 being stirred in an atmosphere of H_2. To the resulting mixture were added 0.34 ml ($5.1 \cdot 10^{-3}$ mole) of ethylenediamine and, after 5 min, a solution of 0.31 g ($1.46 \cdot 10^{-3}$ mole) of the acid (XV) in 3 ml of ethanol. The reaction mixture was stirred at 20°C for 2 h and was then diluted with a saturated solution of NaCl and was extracted with diethyl ether (3 × 50 ml).

After the usual working up of the extract, 0.29 g (93%) of the acid (III) was obtained in the form of a colorless oil, R_f 0.34 [hexane–diethyl ether (1:4)]. PMR spectrum (100 MHz, $CDCl_3$): 1.20 (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 [10, 11].

1-Acetoxytridec-12-en9-yne (XVI). A mixture of 12.0 g ($61.8 \cdot 10^{-3}$ mole) of the alcohol (X), 126 ml of dry Py, and 54 ml of Ac_2O was kept at room temperature for 24 h and was then evaporated; the residue was dissolved in 300 ml of diethyl ether, and this solution was washed successively with 10% HCl and saturated NaCl solution, dried with $MgSO_4$ and evaporated. The residue was chromatographed (SiO_2, hexane–diethyl ether (9:1)), to give 11.8 g (81%) of the acetate (XVI), n_D^{23} 1.4629. IR spectrum (ν, cm^{-1}): 920, 1000, 1645 and 3090 (CH=CH_2), 1250 and 1745 (OAc), 2220 (C≡C). PMR spectrum (100 MHz, $CDCl_3$): 1.3-1.75 (m, 12H, CH_2), 2.05 (s, 3H, CH_3CO), 2.24 (m, 2H, H-8), 2.87-3.0 (m, 2H, H-11), 4.06 (t, 2H, J = 6.5 Hz, H-1), 5.0-5.4 (m, 2H, H-13), 5.65-6.05 (m, 1H, H-12).

12-Acetoxydodec-3-ynoic Acid (XVII). At 5°C, 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 7.1 g ($30 \cdot 10^{-3}$ mole) of the enynic acetate (XVI) in 100 ml of cyclohexane and 10 ml of AcOH until 1.44 g ($30 \cdot 10^{-3}$ mole) of O_3 had been absorbed. The subsequent working up, similar to that described in the synthesis of the acetoxy acid (XIV), gave 6.4 g (84%) of compound (XVII) in the form of a colorless oil, R_f 0.42 (hexane–diethyl ether (1:3)). IR spectrum (ν, cm^{-1}): 1710 and 2400-3600 (CO_2H), 1245 and 1740 (OAc), 2220 (C≡C). PMR spectrum (100 MHz, $CDCl_3$): 1.2-1.8 (m, 12H, CH_2), 2.06 (s, 3H, CH_3CO), 2.2 (m, 2H, H-5), 3.32 (t, 2H, J = 2.2 Hz, H-2), 4.06 (t, 2H, J = 6.5 Hz, H-12).

12-Hydroxydodec-3-ynoic Acid (XVIII). A mixture of 0.9 g ($3.54 \cdot 10^{-3}$ mole) of the acetoxy acid (XVII) and 4.8 g ($34.8 \cdot 10^{-3}$ mole) of K_2CO_3 in 10 ml of MeOH was heated at 50°C for 2 h and was then acidified with 10% HCl to pH ≤ 3 and extracted with diethyl ether (3 × 100 ml). The extract was washed with saturated NaCl solution, dried with $MgSO_4$, and evaporated. This gave 0.71 g (95%) of the hydroxy acid (XVIII) in the form of a colorless oil, R_f 0.29 [hexane–diethyl ether (1:4)]. IR spectrum (ν, cm^{-1}): 1060 (C–O), 1715 and 2400-3600 (CO_2H, OH), 2260 (C≡C). PMR spectrum (100 MHz, $CDCl_3$): 1.2-1.8 (m, 12H, CH_2), 2.2 (m, 2H, H-5), 3.31 (t, 2H, J = 2.2 Hz, H-2), 3.65 (t, 2H, J = 6.3 Hz, H-12), see [5].

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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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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