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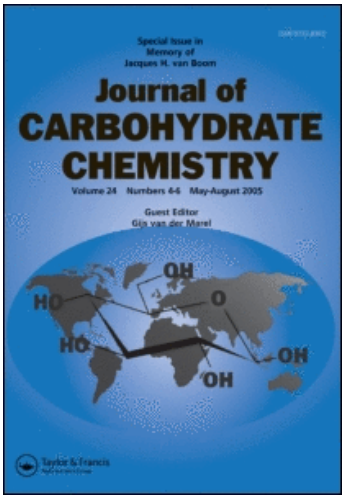

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Wen-Lian Wu; Yu-Lin Wu

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COMMUNICATION

A CONCISE SYNTHESIS OF THE NATURAL MOSQUITO OVIPOSITION ATTRACTANT PHEROMONE FROM D-GLUCOSE

Wen-Lian Wu and Yu-Lin Wu*

Shanghai Institute of Organic Chemistry
Academia Sinica, Shanghai 200032, China

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The major component of the oviposition attractant pheromone of the mosquito *Culex pipiens fatigans* was shown to be (-)-(5*R*, 6*S*)-6-acetoxy-5-hexadecanolide (**1**).[1] For the chemical synthesis of this optically active pheromone,[2] carbohydrates such as D-mannitol[2i] and 2-deoxy-D-ribose[2l] have been utilized as chiral templates. In this laboratory the natural pheromone has been synthesized from (*S*)- and (*R*)-*O*,*O*-isopropylideneglyceraldehyde independently, using diastereoselective dihydroxylation as the key step.[2m] We now describe an enantiospecific synthesis of the pheromone from D-glucose.

2,3-*O*-Ethylidene-D-erythrose (**2**), which can be easily prepared as an anomeric mixture in three steps from D-glucose,[3] was treated with triphenylnonylphosphorane in tetrahydrofuran to afford a mixture of alkenes (**3**)[4] in 95% yield (Scheme 1). Without separation of the geometrical isomers, the alcohol (**3**) was converted to aldehyde (**4**) in 89% yield by Collins' oxidation.

Addition of the appropriate three carbon unit was achieved by a Wittig reaction[5] of aldehyde mixture (**4**) with triphenyl(2-carboxyethyl)phosphorane in THF-DMSO (4:1) at -5 °C. Carboxylic acid (**5**) was obtained in 69% yield after chromatography. Simultaneous hydrogenation of the two double bonds in the presence of palladium on carbon gave (5*R*, 6*S*)-5,6-*O*-ethylidene-5,6-dihydroxyhexadecanoic acid (**6**). Finally, removal of the ethylidene protecting group and subsequent lactonization in aqueous trifluoroacetic acid (90%) furnished the known hydroxylactone (**7**), $[\alpha]_D^{20}$-12.4° (c 0.6, $CHCl_3$). Acetylation of **7** gave the natural pheromone in almost quantitative yield; $[\alpha]_D^{20}$-37° (c 0.4, $CHCl_3$). The spectral properties (IR, ^{1}H-NMR, MS) of **1** were identical with those reported in the literature.[2i]

In conclusion, a concise enantiospecific synthesis of the natural misquito oviposition attractant pheromone has been achieved from the most readily available carbohydrate, D-glucose.

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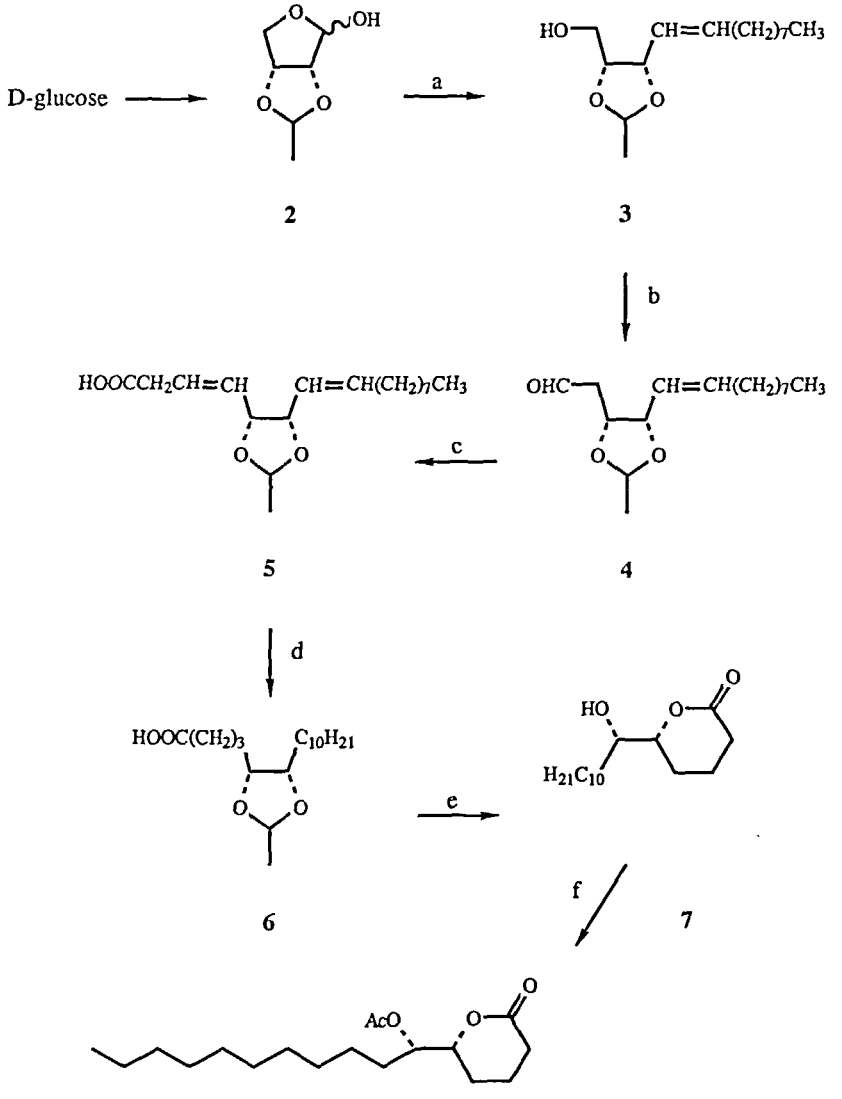

(-) - (5*R*, 6*S*) - **1**

Reagents and conditions: a, $Ph_3P^+C_9H_{19}Br^-$, n-BuLi, THF; b, CrO_3-2pyr., CH_2Cl_2; c, $Ph_3P^+CH_2CH_2CO_2HCl^-$, n-BuLi, THF-DMSO (4:1); d, H_2, Pd-C, EtOH; e, CF_3CO_2H-H_2O (9:1); f, Ac_2O, Pyridine, CH_2Cl_2.

Scheme 1

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REFERENCES AND FOOTNOTES

1. B.R. Laurence, K. Mori, T. Otsuka, J.A. Pickett, L.J. Wadhams, *J. Chem. Ecol.*, **11**, 643 (1985).

2. For the (5*R*, 6*S*)-isomer:
   a) C. Fuganti, P. Grasselli, S. Serri, *J. Chem. Soc., Chem. Comm.*, 1285 (1982).
   b) K. Mori, T. Otsuka, *Tetrahedron*, **1983**, *39*, 3267.
   c) T. Sato, M. Watanabe, N. Honda, T. Fujisawa, *Chem. Lett.*, 1175 (1984).
   d) G.Q. Lin, H.J. Xu, B.C. Wu, G.Z. Guo, W.S. Zhou, *Tetrahedron Lett.*, **26**, 1233 (1985).
   e) K. Machiya, I. Ichimoto, M. Kirihata, H. Ueda, *Agric. Biol. Chem.*, **49**, 643 (1985).
   f) N.C. Barua, R.R. Schmidt, *Tetrahedron*, **42**, 4471 (1986).
   g) P. Prasit, J. Rokach, *J. Org. Chem.*, **53**, 4421 (1988).
   h) K.Y. Ko, E.L. Eliel, *J. Org. Chem.*, **51**, 5353 (1986).
   i) G.Q. Lin, Y.Y. Jiang, G.Z. Guo, K.M. Xia, *Acta Chimica Sinica*, **45**, 602 (1987).
   j) W.S. Zhou, J.F. Cheng, G.Q. Lin, *ibid*, **46**, 274 1988).
   k) T. Kamitani, M. Tubuki, Y. Tatsuzaki, T. Honda, *Heterocycles*, 27(9), 2107 (1988).
   l) S.K. Kang, I.H. Cho, *Tetrahedron Lett.*, **30**, 743 (1989).
   m) M.L. Wu, Y.L. Wu, *J. Chem. Research (S)*, 113 (1990); *J. Chem. Research (M)*, 0866 (1990).
   For the (5*R*, 6*S*)-isomer:
   n) Y. Masaki, K. Nakata, K. Kaji, *Chem. Lett.*, 1835 (1983).
   o) S.K. Kang, D.S. Shin, *Bull. Korean Chem. Soc.*, **7**, 308 (1986).
   p) B.J. Wakefield, *J. Chem. Soc., Chem. Comm.*, 303 (1989).
   q) M. Yamaguchi, I. Hirao, *J. Chem. Soc., Chem. Comm.*, 202 (1984).
   r) C.W. Jeffold, D. Jaggi, J. Boukoralas, *Tetrahedron Lett.*, **27**, 4011 (1986).
   s) B.R. Laurence, J.A. Pickett, *J. Chem. Soc., Chem. Comm.*, 59 (1982).

3. J.W. Van Cleve, C.E. Rist, *Carbohydr. Res.*, 4, 82 (1967).

4. Satisfactory spectral data were obtained for the new compounds in accord with the structure. Selected spectral data are as follows:

   3: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.28 (m, 12H), 1.46 (d, J=4.8Hz, 3H), 2.0-2.2 (m, 2H), 3.58 (m, 2H), 4.14 (m, 1H), 4.86 (dt, J=1, 6.8Hz, 1H), 5.11 (q, J=4.8Hz, 1H), 5.48-5.80 (m, 2H); IR (neat) 3400, 1600 cm^{-1}; MS (m/e) 257 (M^++1).

   4: ^{1}H NMR (200 MHz), $CDCl_3$) δ 0.90 (t, 3H), 1.28 (m, 12H), 1.56 (d, J=4.8Hz, 3H), 2.10 (m, 12H), 4.27 (dd, J=7.6, 3.6Hz, 1H), 5.03 (dd, J=8, 7.6Hz, 1H), 5.24 (q, J=4.8Hz, 1H), 5.35 (m, 1H), 5.72 (m, 1H), 9.52 (d, J=3.5Hz, 1H); IR (neat) 1740 cm^{-1}.

   5: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 12H), 1.56 (d, J=4.8Hz, 3H), 2.10 (m, 2H), 3.10-3.45 (m, 2H), 4.14 (m, 1H), 4.75 (m, 1H), 5.0 (q, J=4.8Hz, 1H), 5.30-6.30 (m, 4H), 9.80 (br, COOH); IR (neat) 3500-2500 (br), 1720 cm^{-1}; MS (m/e) 309 (M^+-1).

   6: ^{1}H NMR (60MHz, CCl_4) δ 0.90 (t, 3H), 1.30-1.60 (m, 21H), 1.60-2.10 (m, 4H), 2.40 (m, 2H), 3.85-4.10 (m, 2H), 4.95 (q, 1H); IR (neat) 3500-2500 (br), 1710 cm^{-1}; MS (m/e) 315 (M^++1).

5. S.R. Baker, D.W. Clissold, *Tetrahedron Lett.*, 29, 991 (1988).

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