

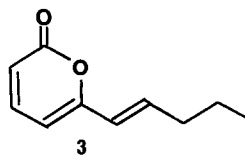
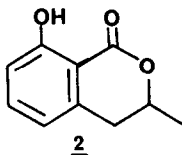
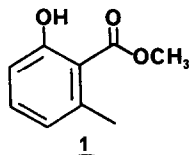
E-6-(1-PENTENYL)-2H-PYRAN-2-ONE FROM
CARPENTER ANTS (Camponotus spp.)

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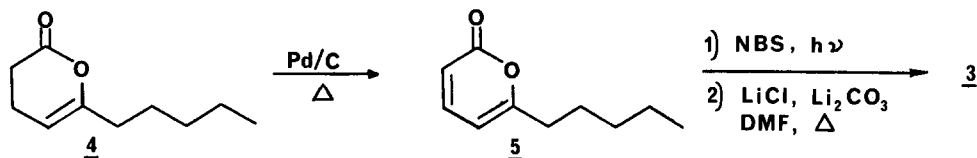
Summary. A novel synthesis of the title compound, 3, is reported along with its identification as a component of the male mandibular gland secretion of some carpenter ants.

Ten years ago the male mandibular gland secretions of the carpenter ants Camponotus pennsylvanicus, C. herculeanus, and C. noveboracensis were found to contain methyl 6-methylsalicylate (1), mellein (2) and 10-methyldodecanoic acid.¹ A fourth component ($m/z=164(M^+)$), which remained unidentified, was also observed in these secretions.¹ Recently, a component of the queen recognition pheromone of the imported fire ant, Solenopsis invicta, has been identified as E-6-(1-pentenyl)-2H-pyran-2-one (3).²



Since the published mass spectrum of 3 was quite similar to that observed for the unidentified Camponotus compound, an authentic sample of 3 was obtained by the following straightforward synthesis for direct comparison. Dehydrogenation of 4-decene-5-olide(4)³ with 10% Pd/C in refluxing cymene⁴ gave 6-pentenyl-2H-pyran-2-one (5) in 60% yield (silica gel chromatography: ir, 1745, 1630, 1555, 1245, 1085, and 800cm⁻¹; nmr δ =7.31(1H, d of d, J=7, 9Hz, H-4), 6.19 (1H, d, J=9Hz, H-3), 6.03(1H, d, J=7Hz, H-5); ms, m/z (rel %) 166(M⁺, 38), 138(10), 110(40), 95(100), 82(30), 81(35), and 68(20).⁵ A CCl₄ solution of 5 containing 1 equiv. of N-bromo-succinimide was irradiated with a 500 watt tungsten lamp for 15 min. Following filtration and removal of the solvent, the residue was taken up in DMF and heated to reflux for 30 min. in the presence of 6 equiv. of LiCl and 6 equiv. of Li₂CO₃.⁶ The resulting mixture was partitioned between ether and water to provide 3 (ms, m/z (rel %) 164(M⁺, 65), 136(20), 135(12), 122(77), 121(14), 110(45), 107(100), 95(90), 94(95), 81(35), 79(53), 77(38), 57(32), 55(60), 43(28), and 41(40)) from the ether layer as the major volatile product⁷ in ca. 70% yield from 5. Pure

samples of 3 could be conveniently obtained by preparative glc; the ir and nmr spectra of synthetic 3 were identical to those reported previously.^{2,8}



The CH_2Cl_2 extracts of 346 male *C. pennsylvanicus* heads, collected in Athens, Georgia, contained 1, 2, and 10-methyldodecanoic acid as well as 3, which had a glc retention time (SP-1000) and mass spectrum identical with those of synthetic 3. Although 3 occurs in *S. invicta* in the presence of structurally dissimilar concomitants,² in the unrelated *Camponotus* species, both 2 and 3 can be envisioned as arising from the same polyketide decanoic acid precursor.

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References.

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2. J.R. Rocca, J.H. Tumlinson, B.M. Glancey, and C.S. Lofgren, *Tetrahedron Lett.*, **24**, 1889 (1983).
3. P. Haverkamp Begeman, V. Lamberti, and W.T. Weller, *Rec. Trav. Chim.*, **86**, 1335 (1967).
4. G.R. Petit, D.C. Fessler, K.D. Paull, P. Hofer, and J.C. Knight, *J. Org. Chem.*, **35**, 1398 (1970).
5. IR spectra were obtained using a Perkin-Elmer 257 grating infrared spectrophotometer; NMR spectra were obtained using either a Varian A60-A or a Varian FT-80 instrument; EI mass spectra were obtained at 70eV using a LKB 9000 GC/MS equipped with a 2m x 2mm i.d. glass column packed with 10% SP-1000 on Supelcoport.
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7. Under these conditions, formation of a monobromo 3 ($m/z = 244, 242, 202, 200, 162, \text{ and } 95$) could be minimized to less than 10%.
8. This synthetic sequence can also be applied to the preparation of sibirinone, an eight carbon homologue of 3. See W.S. Trahanovsky, B.W. Surber, M.C. Wilkes, and M.M. Preckel, *J. Am. Chem. Soc.*, **104**, 6779 (1982).

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