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SYNTHESES OF METHYL DIHYDROJASMONATE AND DIHYDROJASMONE FROM A BUTADIENE TELOMER

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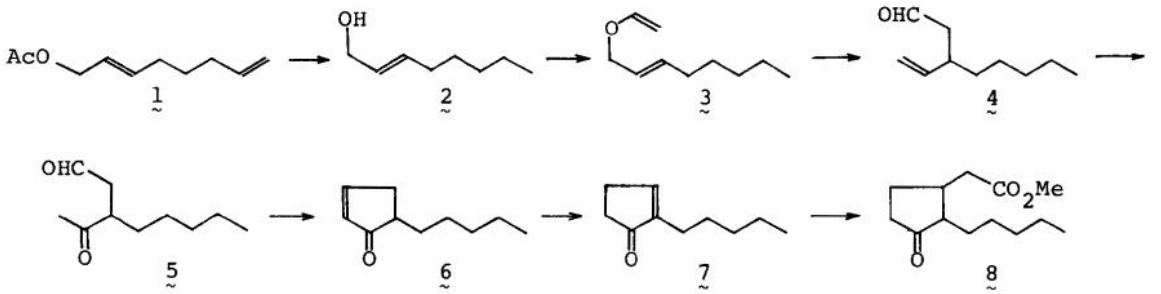
Jasmonoids have been synthesized by the application of new synthetic methods.[1,2] We now wish to report simple syntheses of methyl dihydrojasmonate and dihydrojasmone from a butadiene telomer by applying a palladium catalyzed reaction and [3,3]sigmatropic rearrangement in key steps. As a suitable starting material, 1-acetoxy-2,7-octadiene (1), easily prepared by the palladium catalyzed telomerization of butadiene with acetic acid,[3] was used. The synthesis of methyl dihydrojasmonate (8) was carried out by the following scheme.

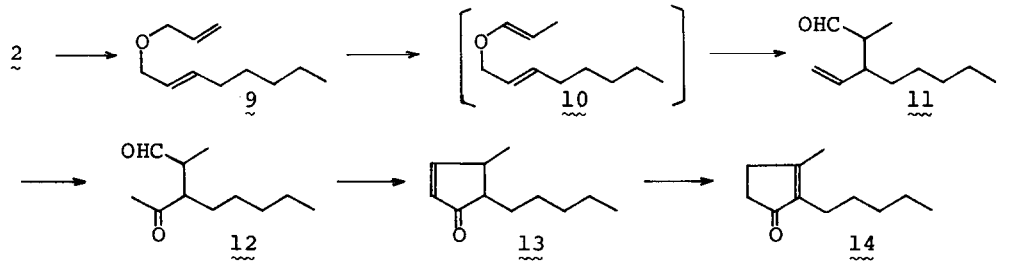


1 2 3 4 5 6 7 8

Terminal double bond of 1 was selectively hydrogenated using $RuCl_2(PPh_3)_3$ as a catalyst as reported before.[4] 2-Octenol (2), obtained after hydrolysis, was converted to 2-octenyl vinyl ether (3) in 71% yield by refluxing in an excess of ethyl vinyl ether in the presence of $Hg(OAc)_2$ for 19 h: NMR (CCl_4) δ 0.88 (t, J = 6 Hz, 3H), 1.05-1.56 (m, 6H), 1.83-2.27 (m, 2H), 3.76-4.24 (m, 4H), 5.38-5.70 (m, 2H), and 6.32 (dd, J = 7 Hz and 15 Hz, 1H). The [3,3]sigmatropic rearrangement of 3 was carried out in a sealed tube at 183-190° for 2 h, to afford 3-vinyloctanal (4) in 79% yield: NMR (CCl_4) δ 0.87 (t, J = 6 Hz, 3H), 1.07-1.57 (m, 8H), 2.17-2.55 (m, 3H), 4.72-5.90 (m, 3H), and 9.53 (t, J = 2 Hz, 1H). The oxidation of the double bond of 4 was carried out in an aqueous DMF using $PdCl_2/CuCl$[5] under oxygen atmosphere at room temperature to give 3-acetyloctanal (5) in 90% crude yield. The keto aldehyde 5, without further purification, was subjected to base-catalyzed aldol condensation. After several trials under various conditions, we found that a mixture of 5% aqueous KOH-THF-Et_2O (1 : 1 : 2) was the best medium and 5-pentyl-2-cyclopentenone (6) was obtained after 48 h reflux in 68% yield from 4: IR (film) 1710 and 1588 cm^{-1}; NMR (CCl_4) δ 0.88 (t, J = 6 Hz, 3H), 1.06-3.10 (m, 11H), 5.89-6.12 (m, 1H), and 7.40-7.64 (m, 1H). On

GLC analysis, 5-pentyl-2-cyclopentenone (6) thus obtained showed only one peak and the retention time was different from that of the isomer 7. The double bond migration to the more substituted side to give 2-pentyl-2-cyclopentenone (7) was carried out by refluxing in a dilute aqueous methanolic KOH for 40 min and pure 2-pentyl-2-cyclopentenone (7) was obtained in 81% yield after chromatographic purification: IR (film) 1706 and 1633 cm^{-1}; NMR (CCl_4) δ 0.88 (t, J = 6 Hz, 3H), 1.07-2.78 (m, 12H), and 7.01-7.29 (m, 1H). The conversion of 7 to dihydrojasmonate (8) is a known reaction,[6] and has been carried out before in this laboratory.[7]

Next the synthesis of dihydrojasmone from 2 was carried out by the similar sequence of reaction. At first allyl 2-octenyl ether (9) was prepared. Heating of the ether 9 in a sealed tube with 0.15 mol% of $RuCl_2(PPh_3)_3$ at 200-205° for 1 h caused the migration of the terminal double bond to form 1-propenyl 2-octenyl ether (10) which then underwent [3,3]sigmatropic rearrangement[8] as soon as it was formed to give 2-methyl-3-vinyloctanal (11) in 61% yield: IR (film) 2685, 1727, 1638, 970, and 916 cm^{-1}; NMR (CCl_4) δ 0.55-2.63 (m, 16H), 4.70-5.97 (m, 3H), and 9.46 (m, 1H). Then the oxidation of the double bond with $PdCl_2/CuCl$[5] was carried out to give the keto aldehyde 12, which was, without purification, subjected to aldol condensation in a mixed solvent of 5% aqueous NaOH-THF-Et_2O (1 : 1 : 2). 2-Pentyl-3-methyl-4-cyclopentenone (13) was obtained in 36% yield after chromatographic purification: IR (film) 1710, 1588, and 1174 cm^{-1}; NMR (CCl_4) δ 0.90 (t, J = 6 Hz, 3H), 1.24 (d, J = 7 Hz, 3H), 1.10-2.90 (m, 10H), 6.07 (dd, J = 1 Hz and 6 Hz, 1H), and 7.48 (dd, J = 2 Hz and 6 Hz, 1H). The double bond migration to the more substituted side with an aqueous methanolic KOH produced dihydrojasmone (14) in 93% yield.[8] IR (film) 1699 and 1644 cm^{-1}; NMR (CCl_4) δ 0.87 (t, J = 6 Hz, 3H), 1.99 (s, 3H), 1.07-2.59 (m, 12H). These spectral data are identical with those of an authentic sample.



References: 1) T. L. Ho, Synth. Commun., 4, 265 (1974). 2) R. A. Ellison, Synthesis, 397 (1973). 3) S. Takahashi, T. Shibano, and N. Hagihara, Tetrahedron Lett., 2451 (1967). 4) J. Tsuji and H. Suzuki, Chem. Lett., 1083 (1977). 5) J. Tsuji, I. Shimizu, and K. Yamamoto, Tetrahedron Lett., 2975 (1976). 6) U. Ravid and R. Ikan, J. Org. Chem., 39, 2637 (1974). 7) J. Tsuji, K. Kasuga, and T. Takahashi, Bull. Chem. Soc. Jpn., submitted. 8) J. M. Reuter and R. G. Salomon, J. Org. Chem., 42, 3360 (1977).

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