Chemistry of Natural Compounds, Vol. 37, No. 1, 2001

CATALYTIC SYNTHESIS OF THE METHYL ESTER OF (9*Z*,12*R*)-12-(METHOXYCARBONYLMETHOXY)-OCTADEC-9-ENOIC ACID

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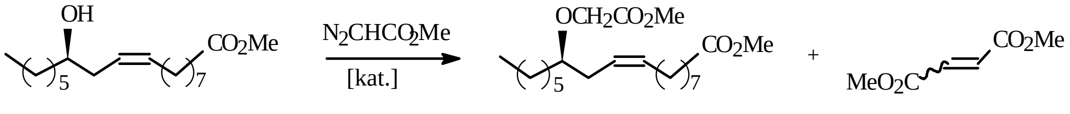
UDC 547.475.124:547.467.2:542.971

Ricinoleic [(9*Z*,12*R*)-hydroxyoctadec-9-enoic] acid is the principal component of castor oil and is considered a promising synthon for the preparation of chiral polyfunctional compounds owing to its availability [1-3]. Furthermore, its derivatives possess a broad spectrum of biological activity [4-7].

Therefore, we developed a synthesis of the methyl ester of (9*Z*,12*R*)-12-(methoxycarbonylmethoxy)octadec-9-enoic acid (**1**) via the reaction of the methyl ester of ricinoleic acid (**2**) and methyldiazoacetate in the presence of catalysts based on Cu, Rh, or Pd. Ester **2** in CH_2Cl_2 at 40°C with 0.5 mol% $Rh_2(OAc)_2$ reacts regioselectively with $N_2CHCO_2CH_3$ to give an optically active addition product of methoxycarbonylcarbene to the O–H bond of **1** in 78% yield. In addition to ester **1**, dimethyl esters of maleic (**3**) and fumaric (**4**) acids, the content of which was <9%, were also isolated from the reaction mixture. It should be noted that carbenes generated from diazoesters can react with enols, as a rule, to add to the O–H bond or to the C=C double bond [8].



2 **1** **3, 4**(Z + E)

The compounds $Cu(CF_3SO_3)_2$, $Rh_2(CF_3CO_2)_4$, $Pd(acac)_2$, and $Pd(OAc)_4$ were less effective as catalysts (Table 1).

Methyl Ester of (9*Z*,12*R*)-12-(Methoxycarbonylmethoxy)octadec-9-enoic Acid (1). A solution of ester **2** (0.2 g, 0.64 mmol) and $Rh_2(OAc)_4$ (1.42 mg, 0.5 mol%) in CH_2Cl_2 (0.5 mL) was added dropwise with heating and stirring to a solution of $N_2CHCO_2CH_3$ (0.064 g, 0.64 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred for 3 h at 40°C. The solvent was evaporated. The solid was chromatographed on an L 40/100-μm silica-gel column with elution by petroleum ether:Et_2O (15:1). Yield of compound **1**, 0.19 g (78%), oil, $[\alpha]_D^{20}$ +11.24° (*c* 16.5, $CHCl_3$).

IR spectrum (ν, cm^{-1}): 1150, 1220, 1465, 1755.

PMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.75 (3H, t, J = 6.5, CH_3-18), 1.10-1.55 (20H, m, CH_2), 1.90 (2H, q, J = 6.42, CH_2-8), 2.10-2.21 (4H, m, CH_2-11, CH_2-2), 3.20-3.30 (1H, m, CH-12), 3.52 (3H, s, CO_2CH_3), 3.61 (3H, s, OCH_3), 4.00 (2H, d, OCH_2CO_2, ^2J 19.23), 5.20-5.40 (2H, m, CH=CH). ^{13}C NMR (75.47 MHz, $CDCl_3$): 13.96 (q, C-18), 22.53 (t, C-17), 24.82 (t, C-3), 25.19 (t, C-14), 27.30 (t, C-13), 29.01 (t, C-4, C-6), 29.06 (t, C-5), 29.33 (t, C-7), 29.41 (t, C-15), 31.32 (t, C-8), 31.73 (t, C-16), 33.65 (t, C-11), 33.95 (t, C-2), 51.25 (q, $CO_2\mathbf{C}H_3$), 51.57 (q, $CO_2\mathbf{C}H_3$), 66.44 (t, $O\mathbf{C}H_2CO_2$), 80.57 (d, C-12), 124.93 (d, C-10), 131.92 (d, C-9), 171.01 (s, $OCH_2\mathbf{C}O_2$), 174.05 (s, $\mathbf{C}O_2CH_3$).

Mass spectrum (EI, 70 eV), *m/z*: 384 [M^+].

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TABLE 1. Effect of Reaction Conditions and Catalyst on Yield of product **1** (CH_2Cl_2, 3 h)

Catalyst, mol%	**2**:$N_2CHCO_2CH_3$	T, °C	Yield of **1**, %	Yield of **3** + **4**, %
$Cu(CF_3SO_3)_2$ (1.0)	1:2	20	31	28
$Cu(CF_3SO_3)_2$ (1.0)	1:1	40	22	31
$Rh_2(OAc)_4$ (0.5)	1:1	14	50	15
$Rh_2(OAc)_4$ (0.5)	1:1	40	78	9
$Rh_2(CF_3CO_2)_4$ (0.5)	1:2	20	57	46
$Pd(acac)_2$ (1.0)	1:1	40	56	13
$Pd(OAc)_2$ (1.0)*	1:2	20	7	45
$Pd(OAc)_2$ (1.0)	1:1	40	7	46

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*Et_2O solvent.

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