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Butenolide annelations using a manganese(III) oxidation. A synthesis of jolkinolide E

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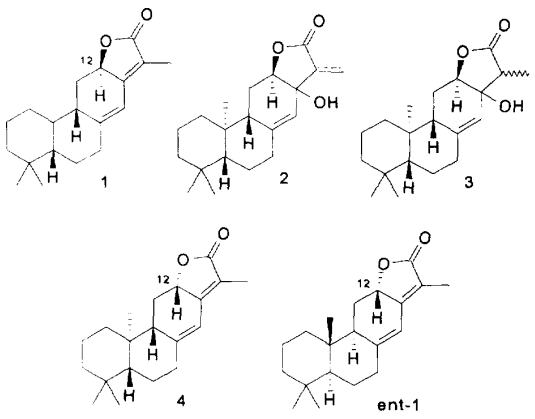
Summary – A general procedure was developed for the annelation of a butenolide to an enone that highlighted a manganese(III) oxidation of an enone. The merit of this procedure was illustrated in a synthesis of (−)-jolkinolide E, *ent*-**1**, from (+)-manool **11**. A potassium permanganate-mediated degradation of **11** and dehydration of an intermediate β-hydroxyketone **12** according to a literature procedure afforded a tricyclic enone **13**. Oxidation of **13** with manganese(III) acetate and chloropropionic acid regio- and stereoselectively furnished a C-12α chloropropionyl ester **14**. An Arbuzov reaction of **14** with triethylphosphite and an intramolecular Horner-Emmons cyclization of the resulting phosphonate **15** gave (−)-jolkinolide E, the structure of which was investigated in detail by NMR. This methodology was also applied to 4,4-dimethylcyclohex-2-en-1-one. This overall approach offers a general solution to the problem of butenolide annelation to enones.

(−)-jolkinolide E / manganese(III) acetate oxidation / butenolide annelation.

Uemura and Hirata [1] first isolated (+)-jolkinolide E **1**, together with jolkinolides A, B, C and D, *from Euphorbia Jolkini Boiss* (Euphorbiaceae). The structural assignment for **1** rested on a correlation with (−)-ferruginol and chemical interconversions among related compounds in the jolkinolide family. However, the C-12α(H) stereochemistry in (+)-jolkinolide E **1** was not rigorously established. The C-12 hydrogen in the ^{1}H NMR spectra of jolkinolide C **2** and its dihydro analog **3** appeared as a broad singlet with half-height band width of 5 Hz consistent with an equatorial hydrogen, and the conversion of dihydrojolkinolide D **3** to **1** suggested that (+)-jolkinolide E **1** possessed the same C-12α(H) stereochemistry as shown in structure **1** in scheme 1. Although this evidence supported the assignment of (+)-jolkinolide E as **1**, the epimeric structure **4** remained a possibility. In this connection, we have undertaken a synthesis of jolkinolide E and a detailed study of the ^{1}H NMR of the naturally occurring material.



Scheme 1

Subsequent to the report on the isolation of (+)-jolkinolide E **1**, Isoe [2] reported a synthesis of racemic **1** and Nakano [3] reported a synthesis of the enantiomer of the natural product, (−)-jolkinolide E *ent*-**1**. In both cases, the syntheses ostensibly supported the C-12α(H) stereochemical assignment originally made by Uemura and Hirata in (+)-jolkinolide E **1**. In addressing the issue of the C-12 stereochemistry, both syntheses relied on a stereoselective epoxidation of an intermediate trimethylsilyl enol ether in order to introduce a C-12 hydroxyl group. For example, as shown in scheme 2 for Nakano's synthesis [3] of *ent*-**1**, the epoxidation of the trimethylsilyl enol ether **5** from the less hindered α-face delivered the α-ketol **6** which has a C-12α hydroxyl group. The α-ketol **6** had ^{1}H NMR data (C-12β hydrogen at δ 4.32 with J = 6 and 13 Hz) and CD measurements (negative π-π^* at 240 nm; positive n-π^* at 323 nm) that supported a pseudoboat conformation **6a** (scheme 3) for ring C in which the C-12α hydroxyl group occupied a pseudoequatorial position. Unfortunately, no base-catalyzed equilibration studies were reported, which might have excluded an alternative pseudochair conformation **6c** for ring C in which the C-12α hydroxyl group occupies a pseudoequato-

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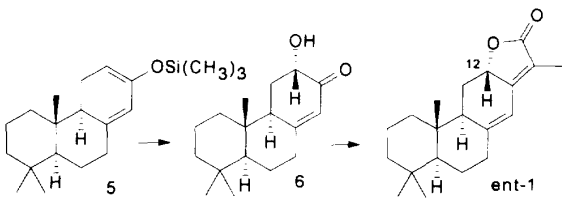
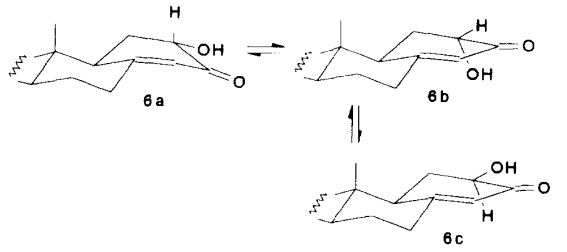


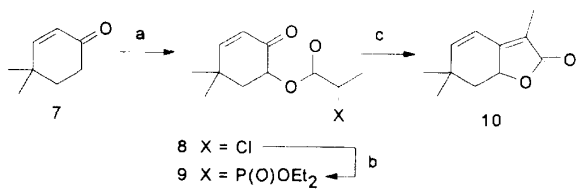
Scheme 2



Scheme 3

rial position. The α-ketol **6** was subsequently converted to (−)-jolkinolide E **ent-1**, which has spectral data in agreement with **1** but an "equal" but opposite optical rotation : for **1**, $[\alpha]_D$ +340 (c = 0.45, $CHCl_3$);and for *ent*-**1**, $[\alpha]_D$ -306 (c = 3.6, $CHCl_3$)).

On the basis of the supportive but limited data in support of the C-12α(H) stereochemistry for **1**, we reinvestigated the synthesis of (−)-jolkinolide E *ent*-**1** using a procedure for the α'-acyloxylation of enones developed in our laboratories [5,6]. In an initial model study shown in scheme 4, the oxidation of 4,4-dimethylcyclohex-2-en-1-one **7** with four equivalents of manganese(III) acetate in combination with 12 equivalents of α-chloropropanoic acid furnished the desired α'-(2-chloropropanoyloxy)enone **8** in good yields as a mixture of diastereomers. The anhydrous manganese(III) acetate used in this oxidation was prepared from manganese(II) nitrate and acetic anhydride and was dried using phosphorus pentoxide under vacuum prior to use. A negligible amount of α'-acetoxylated enone was also obtained in this reaction (5-6% according to GLPC), but separation of the α'-acetoxy and α'-(2-chloropropanoyloxy)ketone **8** was readily accomplished by column chromatography. The Arbuzov reaction of **8** with an excess of triethyl phosphite proceeded

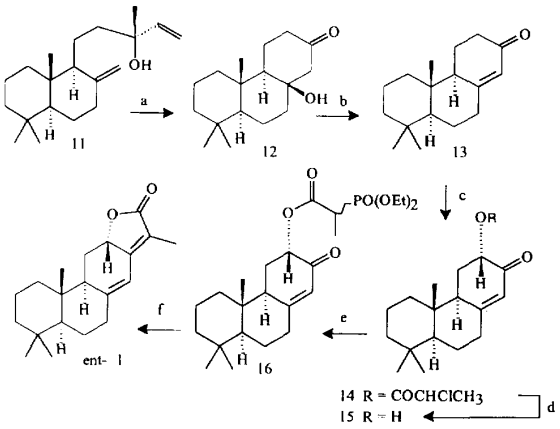


a : 2-chloropropanoic acid, $Mn(OAc)_3$, benzene, reflux (61%); b : $P(OC_2H_5)_3$, reflux (51%); c : NaH, THF, reflux (68%).

Scheme 4

in 51% yields to give the phosphonate **9**. An intramolecular Horner-Emmons cyclization [4] of **9** with sodium hydride in THF gave the desired butenolide **10** in 68% yields.

With the successful completion of this model study, attention was focused on the synthesis of (−)-jolkinolide E *ent*-**1** using the same procedure. As shown in the scheme 5, the oxidation of (+)-manool **11** with potassium permanganate [7] and the dehydration of the intermediate 8β-hydroxypodocarpan-13-one **12** gave podocarp-8(14)-en-13-one **13** [8]. The manganese(III) oxidation of **13** using four equivalents of manganese(III) acetate in combination with 12 equivalents of 2-chloropropanoic acid led regioselectively to the α'-(2-chloropropanoyloxy)enone **14** in 43% yields as a mixture of diastereomers at the acyclic chiral center. The presence of this epimeric mixture at the acyclic position was not a problem since this stereocenter was ultimately removed in the butenolide annelation step.



a : $KMnO_4$, acetone (12%); b : H_3O^+, MeOH, reflux (45%); c : 2-chloropropanoic acid, $Mn(OAc)_3$, benzene, reflux (43%); d : 2 N NaOH, MeOH (87%); e : $P(OC_2H_5)_3$, reflux (51%); f : NaH, THF, reflux (42%).

Scheme 5

The C-12 stereochemistry of the 2-chloropropanoyloxy group in **14** was uncertain at this point, but was later assigned the α-orientation on the basis of its conversion to *ent*-**1**. The ^1H NMR spectrum of **14** displayed the C-12β(H) hydrogen at δ 5.30 as a doublet of doublets ($J_{11\alpha,12\beta}$ = 14 Hz and $J_{11\beta,12\beta}$ = 7 Hz, and saponification [9] of **14** provided the α'-hydroxyenone **15** [7] which also displayed the C-12β(H) hydrogen at δ 4.23 as a doublet of doublets with similar coupling constants. At this stage, this data would support either the C-12β(H) stereochemistry, in which the enone ring occupies a pseudoboat conformation (*eg*, the ester of **6a**), or the C-12α(H) stereochemistry, in which the enone ring occupies a pseudochair conformation (*eg*, the ester of **6c**).

The initial reaction between the manganese(III) acetate and 2-chloropropanoic acid presumably resulted

in a mixed manganese(III) complex, which has both acetate and chloropropionate ligands. This mixed manganese(III) acetate may interact with the enone to form a metal enolate, analogous to the enol-lead triacetate intermediate proposed by Corey and Schaefer [10] for the α-acetoxylation reaction of ketones. Other studies in our laboratories, in which pure manganese(III) carboxylates (eg, manganese(III) propanoate, etc) were prepared and applied to the oxidation of enones failed to produce the desired α-acyloxyenones. Several explanations could be advanced to explain these observations. Pure manganese(III) carboxylates that have ligands other than acetate may have different structures and hence different reactivities relative to manganese(III) acetate. Mixed manganese(III) carboxylates that have acetate and some other carboxylate ligand may form prior to reaction with the enone and possess the reactivity and structure of manganese(III) acetate. Alternatively, manganese(III) acetate may interact with the enone to form a metal enolate, and this acetoxymanganese(III) enolate may subsequently undergo rapid ligand exchange with the excess 2-chloropropanoic acid before giving the α'-(chloropropanoyloxy)enone. Until we know the structures of these presumed mixed manganese(III) complexes or even manganese(III) enolates, which thus far have eluded our efforts at crystallization, the explanation for the observed formation of the α'-(propanoyloxy)enone **14** from enone **13** using manganese(III) acetate and 2-chloropropanoic acid must be regarded as tentative.

Completion of the synthesis of (−)-jolkinolide E *ent*-**1** involved an Arbuzov reaction of α-chloropropionyloxy enone **14** with an excess of triethyl phosphite to give the corresponding phosphonate **16**. The cyclization of **16** with sodium hydride in THF gave *ent*-**1** in 42% yields. The physical and spectral properties of *ent*-**1** were in agreement with values in the literature with the exception of the specific rotation [1,2], and in full agreement with another report [3] on the synthesis of the (−)-enantiomer.

A detailed ^{1}H NMR study of jolkinolide E *rac*-**1** was undertaken to resolve the stereochemical question at C-12. In the COSY HH NMR spectrum, the H-12 proton at δ 4.87 displayed three couplings. The assignment of the small, long-range coupling ($J_{12,18}$ = 1.5 Hz) to the vinylic methyl group was obvious. The remaining two couplings to the equatorial H-11e proton at δ 2.65 and axial H-11 a proton at δ 1.50 were consistent with the general notion that equatorial protons appear at lower fields than axial protons. A detailed analysis of observed coupling constants, particularly $J_{9,11e}$ and $J_{9,11a}$, with coupling constants calculated from dihedral angles from an MM$^+$ minimized structure (table I) was only consistent with structure **1**. The coupling constants calculated from dihedral angles from an MM$^+$ minimized structure for the C-12 epimeric structure **4** were $J_{9,11e}$ = 5.8 Hz (Φ = 48°) and $J_{9,11a}$ = 12.7 Hz (Φ = 170°) and these values were not in agreement with observed J values (table I). In summary, this work has demonstrated the value of a manganese(III) oxidation for the annelation of a butenolide to an enone and, in conjunction with NMR studies, confirmed the structure of (−)-jolkinolide E *ent*-**1**.

Table I. A summary of observed and calculated coupling constants and dihedral angles for jolkinolide E **1**.

Proton pair	Dihedral angle (Φ)	$J_{calculated}$	$J_{observed}$
H-9, H-11a	34°	$J_{9,11a}$ = 8.8 Hz	$J_{9,11a}$ = 9 Hz
H-9, H-11e	84°	$J_{9,11e}$ = 2 Hz	$J_{9,11e}$ =< 1 Hz
H-11a, H-11e	–	–	$J_{11a,11e}$ = 13.9 Hz
H-11a, H-12	173°	$J_{11a,12}$ = 12.8 Hz	$J_{11a,12}$ = 13.3 Hz
H-11e, H-12	58°	$J_{11e,12}$ = 4.3 Hz	$J_{11e,12}$ = 6 Hz

Experimental section

General

All reagents were of commercial quality, and reagent quality solvent were used without further purification. IR spectra were determined on a Philips model PU9700 spectrometer. ^{1}H NMR spectra were determined on a Bruker AC 80 MHz FT, AC 200 MHz and Varian 400 MHz FT spectrometers. GC analyses were determined on a HP 5890 gas chromatograph. Mass spectra were obtained on VGTrio2 spectrometer at an ionization energy of 70 eV. Optical rotation values were measured with a Perkin Elmer P241 polarimeter. Elemental analyses were performed at the Middle East Technical University Analysis Center. Molecular mechanics calculations were performed with Hyper Chem software for computational chemistry and molecular modeling from Autodesk.

6-[(2-Chloropropanoyl)oxy]-4,4-dimethylcyclohex-2-en-1-one **8**

A mixture of manganese(III) acetate (2.12 g, 10 mmol) and 2-chloropropanoic acid (3.24 g, 30 mmol) in benzene (40 mL) was refluxed for 1 h in a Dean-Stark trap. The mixture was cooled, and compound **7** (0.3 g, 2.5 mmol) was added. The mixture was refluxed for 24 h, cooled to 25°C, diluted with EtOAc, washed with 1 M aqueous HCl, satured aqueous $NaHCO_3$ and brine, and dried over anhydrous $MgSO_4$. The crude product was chromatographed on preparative thick-layer chromatography silica-gel F-254 plates (EtOAc/hexane 1:3) to afford **8** (0.351 g, 61%) as an oil.

IR (film) : 1 730, 1 660, 1 600 cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 0.97 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 2.12-2.24 (m, 2H, CH_2), 4.52 (q, 1H, CHCl), 5.50 (dd, 1H, J = 5.8 and 12.4 Hz, C-6 H), 5.86 (d, 1H, J = 10 Hz, C-2 vinylic H), 6.70 (d, 1H, J = 10 Hz, C-3 vinylic H).

Anal calc for $C_{11}H_{15}O_3Cl$: C, 57.26; H, 6.55. Found : C, 57.56; H, 6.41.

6-(2-(Diethoxyphosphinoyl)propanoyloxy)-4,4-dimethylcyclohex-2-en-1-one **9**

A mixture of **8** (0.575 g, 2.5 mmol) and triethyl phosphite (1.3 g, 8 mmol) was refluxed under argon for 3 h. The reaction was monitored by TLC on silica gel (EtOAc/hexane 1:1). During this time, an additional triethyl phosphite (1.3 g, 8 mmol) was added at 1 h intervals. The excess triethyl phosphite was removed by distillation under vacuum, and the residue was chromatographed on preparative thick-layer chromatography silica-gel F-254 plates (EtOAc/hexane 1:1) to afford **9** (0.423 g, 51%) as an oil.

IR (film) : 1 730, 1 660, 1 610, 1 200 cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 0.99 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.12-1.40 (m, 6H, OCH_2CH_3, 2 CH_3), 1.98 (d, 3H, CH_3), 2.10-2.24 (m, 2H, CH_2), 3.85-4.32 (m, 5H, OCH_2, 2 CH_2, CH), 5.41 (m, 1H, C-6 H), 5.86 (d, 1H, J = 10 Hz, C-2 vinylic H), 6.61 (d, 1H, J = 10 Hz, C-3 vinylic H).

MS (EI, 70 eV) m/e 332 (M^+).

3,6,6-Trimethyl-7,7a-dihydrobenzofuran-2(6H)-one **10**

To a suspension of NaH (O.096 g, 4 mmol) (washed with pentane) in anhydrous THF (25 mL) at 25°C under argon was added **9** (0.83 g, 2.5 mmol) dropwise. The mixture was refluxed for 1 h. The reaction was quenched with H_2O and extracted with EtOAc. The organic layer is washed with brine and dried over anhydrous $MgSO_4$. The residue was chromatographed on preparative thick-layer chromatography silica-gel F-254 plates (EtOAc/hexane 1:5) to afford **10** (0.303 g, 68%) as an oil.

IR (film) : 1 770, 1 750, 1 610 cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 1.08 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 2.08(s, 3H, CH_3), 2.14-2.23 (m, 2H, CH_2), 5.45-5.65 (m, 1H, CH), 5.81 (d, 1H, J = 9 Hz, C-4 H), 6.54 (d, 1H, J = 9 Hz, C-5 H).

Anal calc for $C_{11}H_{14}O_2$: C, 74.12; H, 7.90. Found C, 74.46; H, 8.02.

8β-Hydroxypodocarpan-13-one **12**

The procedure of Grant and Hodges [7] was repeated using (+)-manool **11** (10.4 g, 36 mmol) in acetone (40 mL) and potassium permanganate (31.6 g, 200 mmol) to give **12** (1.1 g); mp 202-203°C (lit : 204-205°C [7]).

Podocarp-8(14)-en-13-one **13**

To compound **12** (0.8 g, 3 mmol) in methanol (10 mL) was added sulfuric acid (4 mL). The solution was refluxed for 30 min and cooled to 25°C. The product was extracted with ether and purified by column chromatography on silica gel (pentane/ether 20:1) to afford **13** (0.32 g, 45%); mp 62-64°C (lit : 64-66°C [7]).

12α[(2-Chloropropanoyl)oxy]podocarp-8(14)-en-13-one **14**

A mixture of manganese(III) acetate (1.06 g, 5 mmol)[5,6] and 2-chloropropanoic acid (1.62 g, 15 mmol) in benzene (30 mL) was refluxed for 1 h under a Dean-Stark trap. The mixture was cooled to 25°C, and enone **13** (0.307 g, 1.25 mmol) was added. The mixture was refluxed for 12 h and was cooled to 25°C. The product was diluted with EtOAc, washed successively with 1 M aqueous HCl solution, saturated sodium bicarbonate solution, and brine, and dried over anhydrous $MgSO_4$. The crude product was chromatographed on preparative layer Merck silica gel PF-254 plates (EtOAc/hexane 1:10) to afford **14** (0.255 g, 58%). Recrystallization (EtOAc/hexane) gave **14** (0.189 g, 43%); mp 164-166°C.

IR (KBr) : 1 780, 1 660, 1 610 cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 0.88 (s, 3H, C-10 CH_3), 0.92 (s, 3H, C-4 CH_3), 1.04 (s, 3H, C-4 CH_3), 1.72 (d, J = 7.3 Hz, 3H, $CHCl(CH_3)$), 4.51 (q, J = 7.3 Hz, 1H, $CHCl(CH_3)$), 5.30 (dd, 1H, J = 14 Hz and 7 Hz, C-12 H), 5.91 (br s, 1H, vinylic H).

MS (EI, 70 eV) m/e 352 (M^+).

12α-Hydroxypodocarp-8(14)-en-13-one **15**

A literature procedure [8] was repeated using **14** (0.035 g, 0.1 mmol) and 2 N NaOH (2mL) in MeOH to give **15** (0.021 g, 87%; mp 132-133°C (lit [3] mp 134-136°C).

IR (KBr) : 3 400, 1 670, 1 610 cm^{-1}.

^{1}H NMR (CCl_4) : δ 0.88 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 3.40 (br s, 1H, OH), 4.21 (dd, 1H, J = 13 Hz and 6 Hz, C-12 H), 5.81 (br s, 1H, vinylic H).

Anal calc for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found C, 77.94; H, 10.23.

12α-[2-(Diethoxyphosphinoyl)propanoyloxy]podocarp-8(14)-en-13-one **16**

A mixture of **14** (0.35 g, 1.0 mmol) and triethyl phosphite (1.3 g, 8 mmol) were refluxed under argon for 2 h. The reaction was monitored by TLC (silica gel/ether) and during this time, an additional triethyl phosphite (1.3 g, 8 mmol) was added at 1 h intervals. The excess of triethyl phosphite was removed by distillation under vacuum, and the residue was chromatographed on preparative thick-layer chromatography silica-gel F-254 plates (Et_2O) to afford **16** (0.231 g, 51%) as a semi-solid.

IR (film) : 1 720, 1 650, 1 600, 1 200 cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 0.88 (s, 3H, C-10 CH_3), 0.95 (s, 6H, 2 C-4 CH_3), 1.26 (t, J = 8 Hz, 3H, $CHCH_3$), 1.30-1.33 (m, 6H, 2 OCH_2CH_3), 3.86-4.15 (m, 4H, 2 OCH_2CH_3), 5.20-5.22 (m, 1H, CH), 5.81 (s, 1H, vinylic H).

MS (EI, 70eV) m/e 454 (M^+).

*(−)-Jolkinolide E ent-***1**

To a suspension of sodium hydride (0.036 g, 1.5 mmol) (washed with pentane) in anhydrous THF (6 mL) was added **16** (0.30 g, 0.66 mmol). The mixture was refluxed for 30 min. The mixture was cooled, quenched with 5% HCl solution, and extracted with chloroform. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and the residue was chromatographed on preparative thick-layer chromatography silica-gel F-254 plates (EtOAc/hexane 1:5) to afford *ent*-**1** (0.083 g, 42%); mp 188-190°C (lit [2] 192-194°C). $[\alpha]_D^{20}$ = −293.5 (c = 2.1; $CHCl_3$), (lit [3] $[\alpha]_D$ = −306 (c = 3.6, $CHCl_3$)).

IR (KBr) : 1 760, 1 640 cm^{-1}.

^{1}H NMR ($CDCl_3$) : δ 0.85 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 1.83 (broad s, 3H, CH_3), 2.56 (dd, 1H, J = 9 Hz and 1 Hz, C-9 H), 4.87 (dd, 1H, J = 13.3 Hz and 6 Hz, C-12 H), 6.26 (broad s, 1H, J = 1 Hz, C-14 H).

^{13}C NMR ($CDCl_3$), (400 MHz) : δ 8.26 (C-10 CH_3), 16.82 (C-4 CH_3), 19.08, 21.79 (C-4 CH_3), 23.90, 27.56, 33.58 and 41.64 (C-4 and C-10), 33.87 (C-15 CH_3), 37.19, 39.67, 41.95, 51.92 (C-5), 55.31 (C-9), 76.03 (C-12), 113.92 (C-14), 116.22 (C-13), 152.29 (C-15), 156.25 (C-8), 175.36 (C-16).

MS (EI, 70 eV) m/e 300 (M^+).

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References

1 Uemura D, Hirata Y, *Chem Lett* (1974) 819

2 Katsumura S, Isoe S, *Chem Lett* (1982) 1689; Katsumura S, Kimura A, Isoe S, *Tetrahedron* (1989) 45, 1337

3 Nakano T, Aillo MA, *J Chem Res (S)* (1985) 268

4 Donovan SF, Avery MA McMurry JE, *Tetrahedron Lett* (1979), 3287

5 Demir AS, Jeganathan A, Watt DS, *J Org Chem* (1989) 53, 4020; Demir AS, Camkerten N, Akgun H, Tanyeli C, Mahasneh AS, Watt DS, *Synth Commun* (1990) 20, 2279; Demir AS, Sayrac T, Watt DS, *Synthesis* (1990) 1119; Demir AS, Akgun H, Tanyeli C, Watt DS *Synthesis* (1991) 719

6 For a review see, Demir AS, Jeganathan A, *Synthesis* (1992) 235

7 Grant PK, Hodges R *J Chem Soc* (1960) 5274; Schenk HR, Gutmann H, Jeger O, Ruzicka L, *Helv Chim Acta* (1952) 35, 817; Scheidegger U, Schaffner K, Jeger O *Helv Chim Acta* (1962) 45, 400; Bevan CWL, Ekong DEU, Okogun JI, *Chem Soc C* (1968) 1067; Hugel G, Oehlschlager AC, Ourisson G, *Tetrahedron* (1966) Suppl 8, Part I, 203

8 Church RF, Ireland RE, Marshall JA *J Org Chem* (1966) 31, 2526

9 Plattner JJ, Gless RD, Rapoport H, *J Am Chem Soc* (1972) 94, 8613; Liang S, Paquette LA, *Tetrahedron : Asymmetry* (1990) 1, 445

10 Corey EJ, Schaefer JP, *J Am Chem Soc* (1960) 82, 918