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Enantiospecific first total synthesis of (+)-*trans*-α-himachalene☆

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Abstract—An enantiospecific first total synthesis of (+)-*trans*-α-himachalene, one of the eight male specific sesquiterpenes isolated from the crucifer flea beetle *Phyllotreta cruciferae*, starting from the readily and abundantly available monoterpene, (*R*)-carvone, is described.

Flea beetles constitute the largest subfamily of the leaf beetle family *Chrysomelidae*. Adult flea beetles feed on host plant foliage and the larvae typically feed on the roots of the same plant. The group includes both agricultural pests and beneficial species. For example, *Phyllotreta cruciferae* Goeze is a significant pest of canola and rapeseed in the northern prairie areas of the United States and Canada and it also attacks cabbage, horseradish and other crucifers in many regions. On the other hand, *Aphthona flava* Guillebeau, *A. czwalinae*, and *A. cyparissiae* are effective biocontrol agents of the leafy spurge (*Euphorbia esula* L.). In an attempt to discover the possible pheromone components of the flea beetles, the research group of Bartelt[1] investigated volatile constituents from the four species *P. cruciferae*, *A. flava*, *A. czwalinae*, and *A. cyparissiae*, which led to the isolation of eight male specific compounds **1**–**8** exhibiting pheromonal function (Fig. 1). The structure of *trans*-α-himachalene (+)-**1** was established by comparison of the ^{1}H NMR spectral data with that of the optical antipode (−)-**1** obtained (along with various other isomers) from α-himachalene mono and dihydrochlorides (prepared from *cis*-a-himachalene **9**, a major sesquiterpene of the essential oil from the Himalayan deodar, *Cedrus deodara*, Loud.), by the research groups of Dev,[2] de Mayo[3] and Bernardini.[4] Herein, we report the enantiospecific first total synthesis of *trans*-a-himachalene (+)-**1** starting from the readily and abundantly available monoterpene (*R*)-carvone **10**.

The retrosynthetic analysis of *trans*-α-himachalene **1** is depicted in Scheme 1. It was contemplated that the presence of the propionaldehyde and isopropenyl side chains at the C-3 and C-4 positions of methylcyclohexene, for example, **11**, would be ideal for generating hydroxyhimachalene **12** via a carbonyl ene reaction.[5] Initially, the Lewis acid catalyzed Mukaiyama–Michael addition

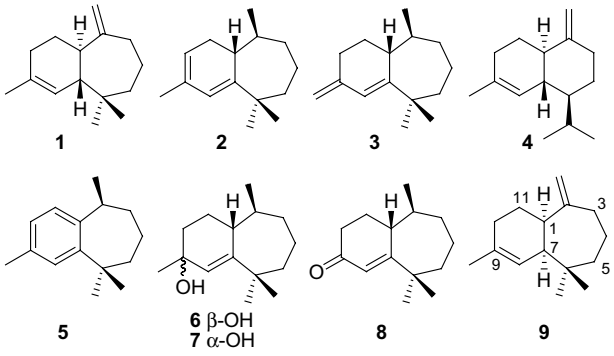
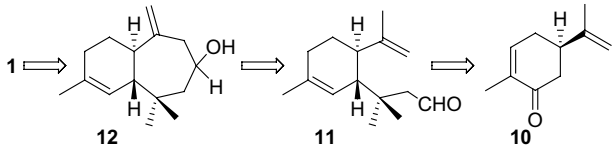


Figure 1.



Scheme 1.

Keywords: Terpene synthesis; Pheromones; Carbonyl ene reaction.

☆ Chiral synthons from carvone, Part 66. For parts 64 and 65, see Ref. 10.

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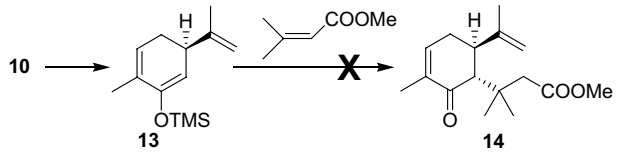
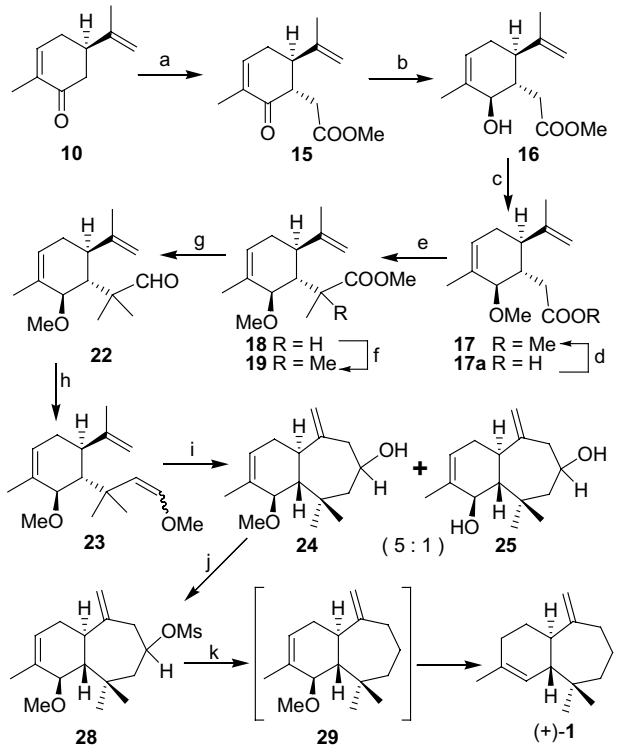


Scheme 2.

reaction[6] of TMS enol ether **13**, derived from (*R*)-carvone **10**, to dimethylacrylate was explored for the generation of the keto ester **14**, but was unsuccessful (Scheme 2).

Consequently, an alternative longer route was investigated (Scheme 3). Generation of the kinetic dienolate of (*R*)-carvone **10** using LDA in THF and alkylation with methyl bromoacetate at −70 °C generated, exclusively, the *trans*-keto ester **15** in 75% yield. The *trans* stereoselectivity is well established in the kinetic alkylation of carvone.[7] Chemo- and stereoselective reduction of the ketoester **15** with sodium borohydride in methanol at −30 °C furnished, exclusively, the hydroxy ester **16**, in 79% yield. Williamson's etherification of the hydroxy ester **16** with sodium hydride and methyl iodide in the presence of a catalytic amount of tetrabutylammonium iodide (TBAI) in refluxing THF furnished a 5:2

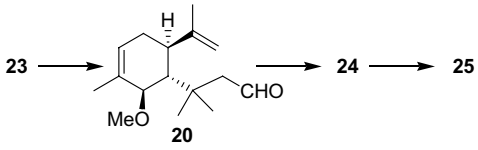


Scheme 3. Reagents, conditions, and yields: (a) LDA, THF, −70 °C, 45 min; $BrCH_2CO_2Me$, 3 h; rt, 6 h, 75%; (b) $NaBH_4$, MeOH, −30 °C, 45 min, 79%; (c) NaH, MeI, TBAI, THF, reflux, 6 h, 72%; (d) CH_2N_2, Et_2O, 0 °C, 90%; (e) LDA, MeI, THF, 0 °C → rt, 6 h; (f) LDA, MeI, THF, HMPT, 0 °C → rt, 6 h, 60% (over two steps); (g) (i) LAH, Et_2O, 0 °C, 2 h, 86%; (ii) PCC, NaOAc, CH_2Cl_2, rt, 1 h 76%; (h) $Ph_3P^+CH_2OMe\ Cl^-$, $K^+\ {}^tAmO^-$, THF, rt, 3 h, 71%; (i) 3 N HCl, THF, rt, 1.5 h, 66%; (j) MsCl, py, CH_2Cl_2, DMAP, rt, 2 h, 71%; (k) Li, liq. NH_3, THF, 33 °C, 45 min, 57%.

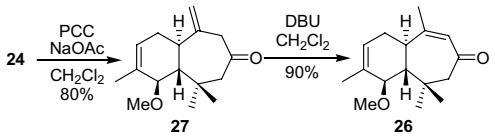
mixture of the methyl ether **17** and the carboxylic acid **17a**. Esterification with an excess of ethereal diazomethane transformed the acid **17a** into the ester **17** in 72% yield.[11] Alkylation of the ester **17** using LDA and methyl iodide in THF at ice temperature furnished a 4:1 epimeric mixture of the α-methyl esters **18** in 90% yield. A second alkylation of the epimeric mixture **18** with LDA and methyl iodide in THF-HMPT at ice temperature furnished the α,α-dimethylated ester **19** in 60% yield (over two steps).[11]

One carbon homologation of the ester **19** to the aldehyde **20** followed by intramolecular carbonyl ene reaction was contemplated for the construction of the himachalene framework. Reduction of the ester **19** with LAH in ether at 0 °C furnished the corresponding alcohol **21** in 86% yield, which on oxidation with PCC and sodium acetate in methylene chloride gave the aldehyde **22** in 76% yield.[11] Wittig reaction of the aldehyde **22** with methoxymethylenetriphenylphosphorane in THF furnished a 1:1 *E*/*Z* mixture of the enol ether **23** in 71% yield. Acid catalyzed hydrolysis of the enol ether **23** in 0.02 M THF solution using 3 N aqueous hydrochloric acid at room temperature generated, instead of the aldehyde **20**, a 5:1 mixture of the bicyclic alcohol **24** and the diol **25**, in 66% yield, which were separated by column chromatography on silica gel.[11] The structures of the alcohols **24** and **25** were deduced from their spectral data. Alcohols **24** and **25** were formed via the acid catalyzed carbonyl ene reaction of the initially formed aldehyde **20**, followed by partial hydrolysis of the allyl methoxy group in **24** (→**25**) under the reaction conditions (Scheme 4). It is worth mentioning that the reaction proceeded in a highly stereoselective manner, and only one stereoisomer was obtained. No attempt was made to assign the stereochemistry of the alcohol moiety in **24** as it is deoxygenated in the next reaction step. In order to confirm the structure of alcohol **24**, it was converted into the enone **26** via the ketone **27**. Thus, oxidation of alcohol **24** with PCC and sodium acetate in methylene chloride furnished the β,γ-unsaturated ketone **27** in 80% yield, which on isomerization with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in methylene chloride generated the enone **26** in 90% yield (Scheme 5).[11] The structure of the enone **26** was established from the spectral data and unambiguously confirmed by single crystal X-ray analysis (Fig. 2).[11]

Next, attention was turned to the conversion of the bicyclic alcohol **24** into *trans*-α-himachalene **1** via reductive deoxygenation of the C-4 hydroxy group and reductive cleavage of the allylic methoxy group. Since Barton's deoxygenation protocol was unsuccessful, it was decided to carry out the deoxygenation[8] of the hydroxy group in



Scheme 4.



Scheme 5.

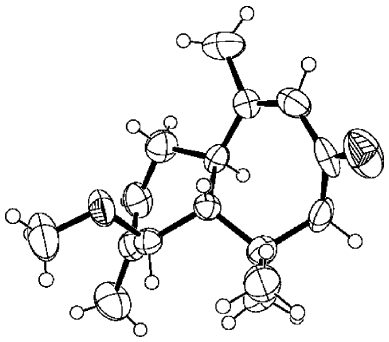


Figure 2. X-ray structure of the enone **26**.

24 via the sulphonate ester **28**. Thus, reaction of alcohol **24** with methanesulfonyl chloride, pyridine, and a catalytic amount of DMAP in methylene chloride furnished the mesylate **28** in 71% yield. Reaction of **28** with lithium in liquid ammonia and THF at −33 °C generated directly, *trans*-α-himachalene[11] **1**, $[\alpha]_D^{25}$ +67 (*c* 1.4, hexane), {lit.[1] $[\alpha]_D$ +50 (*c* 0.008, hexane)}, instead of the methyl ether **29**, via simultaneous reductive demesylation and demethoxylation reactions, in a regioselective manner.[9] Synthetic *trans*-α-himachalene (+)-**1** exhibited ^{1}H NMR spectral data identical to those of the natural sample isolated[1] from the flea beetles, and the ^{13}C NMR data reported[4] for the optical antipode (−)-**1** by Bernardini and co-workers.

In conclusion, we have accomplished the enantiospecific first total synthesis of the natural enantiomer of *trans*-α-himachalene (+)-**1** starting from the readily and abundantly available (*R*)-carvone in 11 steps employing an intramolecular carbonyl ene reaction as the key step. The present sequence in addition to confirming the stereostructure, also established the absolute configuration of the natural product.

Acknowledgements

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9. It is worth mentioning that the reaction did not produce any significant amount of the isomeric himachalene (6,6,9-trimethyl-2-methylenebicyclo[5.4.0]undec-9-ene).[2,3]
10. Part 64: Srikrishna, A.; Satyanarayana, G. *Org. Lett.* **2004**, *6*, 2337; Part 65: Srikrishna, A.; Viswajanani, R.; Dinesh, C. *Ind. J. Chem. Sec. B* **2004**, *43*, 1265.
11. All the compounds exhibited spectral data (IR, ^{1}H and ^{13}C NMR, mass and HRMS) consistent with their structures. Selected spectral data for the ester **17**: $[\alpha]_D^{23}$: +66.6 (*c* 3.5, $CHCl_3$). IR (neat): ν_{max}/cm^{-1} 1739, 1640, 887. ^{1}H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 5.51 (1H, br s, H-4′), 4.74 (2H, s, C=CH_2), 3.82–3.72 (1H, m, C*H*-OMe), 3.61 (3H, s, COOCH_3), 3.17 (3H, s, O–CH_3), 2.39 (1H, d, *J* = 14.1 Hz), 2.30–1.80 (5H, m), 1.66 (6H, s, 2 × olefinic CH_3). ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$, DEPT): δ 173.1 (C, O–C=O), 146.3 (C, *C*=CH_2), 134.6 (C, C-3′), 125.4 (CH, C-4′), 113.5 (CH_2, C=CH_2), 83.2 (CH, CH-OMe), 54.0 (CH_3, O–CH_3), 51.2 (CH_3, $COOCH_3$), 46.7 (CH, C-6′), 37.5 (CH, C-1′), 36.1 (CH_2), 30.8 (CH_2), 19.5 (CH_3) and 18.3 (CH_3) [2 × olefinic CH_3]. Mass: *m*/*z* 238 (M^+, 12%), 164 (33), 149 (35), 133 (50), 123 (25), 105 (47), 98 (100), 91 (35). HRMS: *m*/*z* calcd for $C_{14}H_{22}O_3Na$ (M+Na): 261.1467. Found: 261.1450. For the ester **19**: $[\alpha]_D^{25}$: +94.2 (*c* 6.4, $CHCl_3$). IR (neat): ν_{max}/cm^{-1} 1732, 887. ^{1}H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 5.73 (1H, br s, H-4′), 4.70 (2H, br s, C=CH_2), 3.60 (3H, s, CO_2CH_3), 3.52 (1H, s, C*H*–OMe), 3.20 (3H, s, OCH_3), 2.45 (1H, dd, *J* = 6.9 and 2.7 Hz), 2.40–2.00 (2H, m), 2.00–1.85 (1H, m), 1.74 (3H, s) and 1.72 (3H, s) [2 × olefinic CH_3], 1.18 (3H, s) and 1.11 (3H, s) [2 × CH_3]. ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$, DEPT): δ 177.7 (C, OC=O), 148.8 (C, *C*=CH_2) 134.5 (C, C-3′), 126.6 (CH, C-4′), 111.7 (CH_2, C=CH_2), 78.6 (CH, C-2′), 54.5 (CH_3, OCH_3), 51.3 (CH_3, CO_2CH_3), 46.1 (CH), 45.4 (C, C-2), 42.7 (CH), 29.5 (CH_2, C-5′), 23.4 (CH_3), 23.0 (CH_3), 21.7(CH_3), 19.9 (CH_3). Mass: *m*/*z* 207 (M−CO_2CH_3, 8%), 165 (M−[Me_2C–CO_2CH_3], 30), 149 (45), 133 (90), 123 (50), 114 (45), 109 (50), 102 (100), 98 (90), 93 (40), 91 (40). HRMS: *m*/*z* calcd for $C_{16}H_{26}O_3$ Na (M+Na): 289.1780. Found: 289.1797. For the aldehyde **22**: $[\alpha]_D^{24}$: +88.0 (*c* 7.0, $CHCl_3$). IR (neat): ν_{max}/cm^{-1} 2711, 1722, 1643, 890. ^{1}H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 9.27 (1H, s, O=C–H), 5.63 (1H, s, H-4′), 4.78 (1H, s) and 4.73 (1H, s) [C=CH_2], 3.55 (1H, d, *J* = 5.1 Hz, H-2′), 3.14 (3H, s, OCH_3), 2.40–2.00 (3H, m), 1.90–1.60 (1H, m), 1.71 (3H, s) and 1.68 (3H, s) [2 × olefinic CH_3], 1.02 (6H, s) [2 × CH_3]. ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$, DEPT): δ 202.4 (CH, O=C–H), 148.6 (C, *C*=CH_2), 134.9 (C, C-3′), 125.9 (CH, C-4′), 113.1 (CH_2, C=CH_2), 79.2 (CH, C-2′), 54.7 (CH_3,OCH_3), 49.0 (C, C-2), 46.0 (CH), 43.3 (CH), 30.3 (CH_2, C-5′), 20.7 (CH_3), 20.3 (CH_3), 20.2 (CH_3), 18.2 (CH_3). Mass: *m*/*z* 236 (M^+, 10%), 195 (20), 187 (20), 165 (20), 149 (70), 135 (90), 123

(55), 119 (65), 109 (45), 99 (70), 98 ($C_6H_{10}O$, retro DA fragment, 100), 91 (50). HRMS: *m/z* calcd for $C_{15}H_{24}O_2Na$ (M+Na): 259.1674. Found: 259.1660. For the alcohol **24**: $[\alpha]_D^{24}$: +64.3 (*c* 3.0, $CHCl_3$). IR (neat): ν_{max}/cm^{-1} 3393 (OH), 2926, 1637, 1466, 1444, 1389, 1368, 1188, 1089, 1068, 1032, 931, 889. ^1H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 5.77 (1H, d, $J = 6.6$ Hz, H-10), 4.90 (1H, s) and 4.80 (1H, s) [C=CH_2], 3.96 (1H, br s, H-4), 3.87 (1H, d, $J = 6.3$ Hz, H-8), 3.09 (3H, s, OCH_3), 2.68 (1H, dd, $J = 13.2$ and 3.9 Hz), 2.35–2.00 (3H, m), 1.90–1.70 (3H, m), 1.70 (3H, s, olefinic CH_3), 1.70–1.40 (2H, m), 1.16 (3H, s) and 0.89 (3H, s) [$2 \times CH_3$]. ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$, DEPT): δ 150.5 (C, C-2), 134.8 (C, C-9), 127.9 (CH, C-10), 113.0 (CH_2,C=CH_2), 78.8 (CH, C-8), 66.7 (CH, C-4), 52.4 (CH_2), 51.0 (CH_3, OCH_3), 47.3 (CH), 43.4 (CH), 42.8 (CH_2), 35.8 (C, C-6), 33.2 (CH_2), 31.0 (CH_3), 24.5 (CH_3), 21.0 (CH_3). Mass: *m/z* 250 (M^+, 12%), 218 (10), 147 (18), 133 (20), 119 (32), 105 (30), 99 (20), 91 (35), 49 (100). HRMS: *m/z* calcd for $C_{16}H_{26}O_2Na$ (M+Na): 273.1830. Found: 273.1841. For the diol **25**: $[\alpha]_D^{23}$: +25.5 (*c* 2.0, $CHCl_3$). IR (neat): ν_{max}/cm^{-1} 3353, 1636, 890. ^1H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 5.39 (1H, s, H-10), 4.93 (1H, s) and 4.84 (1H, s) [C=CH_2], 4.00–3.85 (1H, m, H-4), 3.83 (1H, s, H-8), 2.79 (1H, dd, $J = 14.1$ and 6.6 Hz), 2.41 (1H, br t, $J = 11.8$ Hz), 2.17 (1H, d, $J = 14.4$ Hz), 1.91 (1H, d, $J = 11.7$ Hz), 1.79 (3H, s, olefinic CH_3), 1.80–1.60 (3H, m), 1.50–1.05 (3H, m), 1.08 (3H, s) and 0.76 (3H, s) [$2 \times CH_3$]. ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$, DEPT): δ 149.9 (C, C-2), 134.7 (C, C-9), 126.9 (CH, C-10), 112.6 (CH_2, C=CH_2), 67.7 (CH), 66.2 (CH), 49.5 (CH_2), 46.6 (CH), 42.8 (CH_2), 41.5 (CH_2), 34.5 (CH), 34.2 (C, C-6), 28.1 (CH_3), 25.3 (CH_3), 21.3 (CH_3). Mass: *m/z* 236 (M^+, 15%), 185 (20), 175 (20), 161 (30), 147 (75), 135 (43), 133 (45), 121 (46), 119 (75), 109 (80), 105 (70), 91 (100), 73 (75), 69 (70), 49 (90). HRMS: *m/z* calcd for $C_{15}H_{24}O_2Na$ (M+Na): 259.1674. Found: 259.1696. For the enone **26**: $[\alpha]_D^{23}$: +296.1 (*c* 1.8, $CHCl_3$). IR (neat): ν_{max}/cm^{-1} 1656, 1614. ^1H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 5.97 (1H, s, H-3), 5.91 (1H, d, $J = 6.6$ Hz, H-10), 3.47 (1H, s, H-8), 3.20 (3H, s, OCH_3), 2.65–2.50 (1H, m), 2.55 and 2.20 (2H, $2 \times$ d, $J = 11.7$ Hz, H-5), 2.36 (1H, tt, $J = 13.8$ and 2.7 Hz), 2.35–2.15 (1H, m), 2.02 (3H, s, C_2–CH_3), 1.84 (3H, s, C_9–CH_3), 1.90–1.75 (1H, m), 1.13 (3H, s) and 0.77 (3H, s) [$2 \times CH_3$]. ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$, DEPT): 199.9 (C, C=O), 165.8 (C, C-2), 137.9 (C, C-9), 131.7 (CH, C-3), 127.6 (CH, C-10), 79.6 (CH, C-8), 58.9 (CH_3,OCH_3), 57.2 (CH_2, C-5), 55.9 (CH), 39.9 (CH), 34.4 (C, C-6), 27.3 (CH_3), 25.7 (CH_2, C-8), 24.2 (CH_3), 23.6 (CH_3), 22.6 (CH_3). HRMS: *m/z* calcd for $C_{16}H_{25}O_2$ (M+1): 249.1854. Found: 249.1857. For *trans*-α-himachalene **1**: $[\alpha]_D^{23}$: +67 (*c* 1.4, hexane). lit.[1] $[\alpha]_D$: +50.0 (*c* 0.008, hexane) lit.[2] for (−)-**1** $[\alpha]_D$: −39.5. IR (neat): ν_{max}/cm^{-1} 1636, 884. ^1H NMR (500 MHz, $CDCl_3$): δ 5.28 (1H, br s, H-8), 4.76 (1H, s) and 4.68 (1H, s) [C=CH_2], 2.35–2.20 (2H, m), 2.10–1.95 (2H, m), 1.90–1.75 (2H, m), 1.67 (3H, s, olefinic CH_3), 1.75–1.50 (3H, m), 1.50–1.40 (1H, m), 1.37–1.20 (2H, m), 0.96 (3H, s) and 0.70 (3H, s) [$2 \times CH_3$]. ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$, DEPT): δ 155.9 (C, C-2), 134.1 (C, C-9), 124.0 (CH, C-8), 109.9 (CH_2, C=CH_2), 50.7 (CH, C-7), 40.83 (CH, C-1), 40.77 (CH_2), 36.6 (C, C-6), 34.9 (CH_2), 31.9 (CH_2), 31.1 (CH_2), 29.9 (CH_3), 24.3 (CH_3), 23.3 (CH_3), 20.5 (CH_2, C-4). [lit.[4] data: (25 MHz, $CDCl_3$): δ 156.3, 134.8, 123.7, 109.3, 50.6, 40.7, 40.6, 36.3, 34.7, 31.8, 30.9, 29.6, 23.8, 22.8, 20.4]. Mass: ($C_{15}H_{24}$) *m/z* 204 (M^+, 5%), 203 (M−H, 25), 189 (M−Me, 12), 175 (10), 161 (15), 149 (30), 135 (40), 133 (35), 121 (45), 119 (40), 109 (70), 105 (60), 91 (60), 69 (100).

X-ray data for the enone **26**: X-ray data were collected at 293 K on a SMART CCD-BRUKER diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). The structure was solved by direct methods (SIR92). Refinement was done by full-matrix least-squares procedures on F^2 using SHELX-97. The nonhydrogen atoms were refined anisotropically whereas hydrogen atoms were refined isotropically. $C_{16}H_{24}O_2$, MW = 248.37, colorless crystal, Crystal system: orthorhombic, space group: P2(1)2(1)2(1), cell parameters: a = 8.186 (4) Å, b = 10.769 (6) Å, c = 16.594 (9) Å, V = 1462.95 Å^3, $Z = 4$, D_c = 1.128 g cm^{-3}, $F(000)$ = 544.0, μ = 0.07 mm. Total number of l.s. parameters = 168, $R1$ = 0.0773 for 1293 $Fo > 4\sigma(Fo)$ and 0.1797 for all 2652 data. WR2 = 0.1093, GOF = 0.886, Restrained GOF = 0.886 for all data. ORTEP diagram is given in Figure 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 236133).