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Total Synthesis of (±)-Davanone

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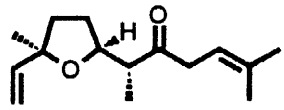
Abstract

The total synthesis of the sesquiterpene (±)-davanone is described. A Lewis acid catalyzed [3+4] annulation reaction of 1,4-pentanedione with bis(trimethylsilyl) enol ether **2** is the key synthetic step. The resulting oxabicyclo[3.2.1]heptanone system can be selectively ring-opened and then elaborated further to (±)-davanone.

Keywords: annulation; oxygen heterocycles; ring transformations; terpenes and terpenoids.

Introduction

The sesquiterpene ketone (+)-davanone (**1**) is the major component of the south Indian plant Artemisa Pallens.[1] It is also found in other plants, for example Tanacetum Vulgare.[2] Davanone (**1**) was first characterized in 1962 by Sipma and van der Wal.[3] Its relative stereochemistry was proposed independently by both Naegeli[4] and Birch[5] through the synthesis of all possible diastereomers and was subsequently proven by Ohloff in 1970.[6]



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(+)-davanone

Davanone (**1**) has been synthesized previously by several groups.[7] However, all of these syntheses were long and only two of them stereoselective with regard to the formation of the *cis*-disubstituted tetrahydrofuran ring.[7,8] High stereoselectivity was achieved by Honda *et al.*[8] *via* an iodo etherification reaction which formed the tetrahydrofuran ring with 21:1 selectivity in favor of the desired *cis*-isomer.

The Lewis acid catalyzed [3+4] and [3+5] annulation reactions of 1,4- and 1,5-dicarbonyl compounds with bis(trimethylsilyl) enol ethers have been demonstrated to be a highly effective method for the construction of functionalized oxabicyclo[3.2.1]heptanones and

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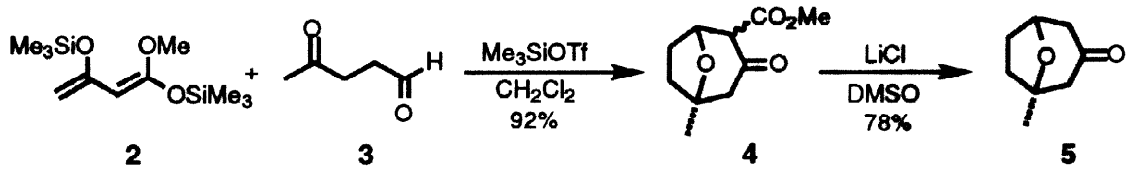
oxabicyclo[3.3.1]octanones, respectively.[9-15] This method has been used successfully in the synthesis of several natural products, including dactylol[16] and furanether B.[17] A major advantage of constructing *cis*-disubstituted furan and -pyran systems by means of ring opening oxabicyclo[3.2.1] and -[3.3.1] systems is the control of stereochemistry achieved with regard to formation of the cis-disubstituted heterocyclic ring itself. Formation of a *trans*-substituted oxabicyclo ring system is impossible because of ring strain. In addition, these systems provide sterically defined, reasonably rigid platforms that can be readily embellished with additional stereocenters. In particular, they show a high propensity for axial ("exo") alkylation adjacent to the ketone carbonyl. By combining these advantages, an efficient route to (±)-davanone has been developed and is reported herein.

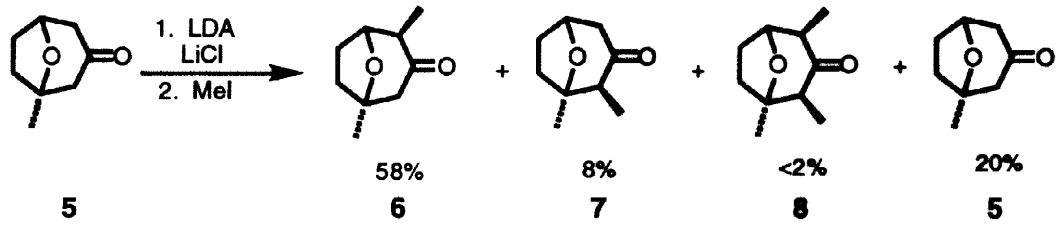
Results and discussion

The current study began with the annulation reaction of bis(trimethylsilyl) enol ether **2** and 1,4-pentanedione (**3**). Exposure of a mixture of **2** and **3** to a catalytic quantity of trimethylsilyl triflate at -50 °C in dry dichloromethane furnished oxabicyclo[3.2.1]heptanone **4** in high yield.[11] Although irrelevant in this synthesis (the carboxymethyl group is removed in the next step) it is noteworthy that this annulation reaction proceeded with very high regioselectivity (>99:1). Keto ester **4** was decarboxylated under Krapcho[18-19] conditions to afford ketone **5**.

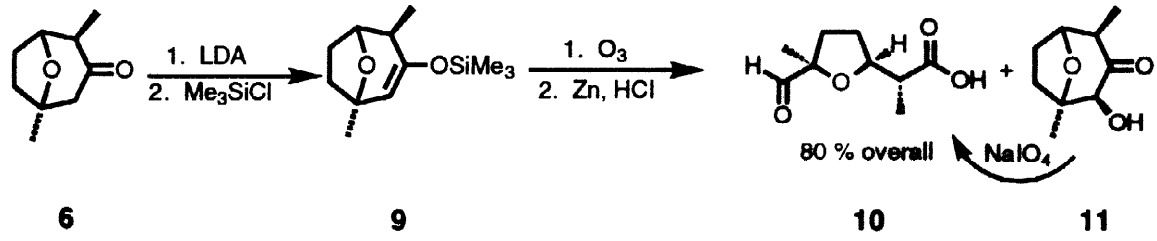


2 **3** **4** **5**

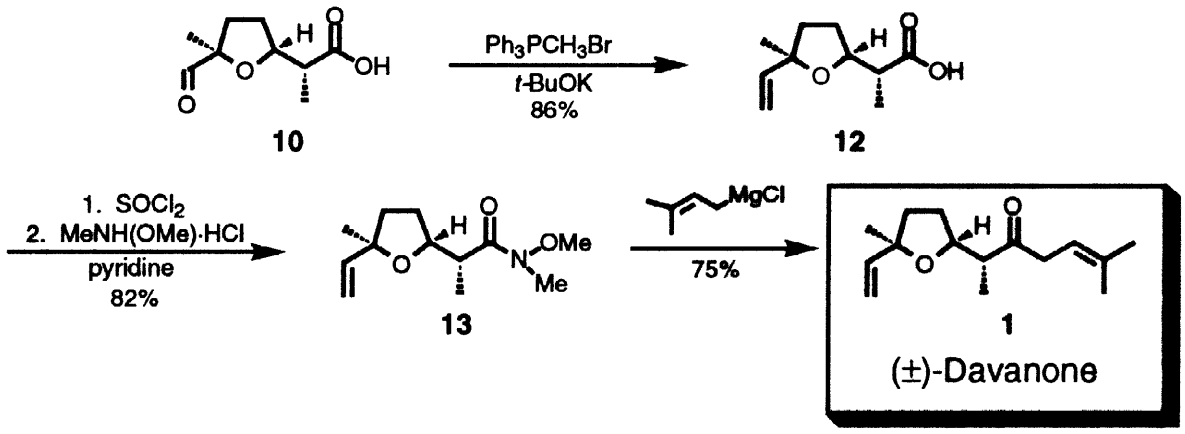
Intermediate **5** could be selectively methylated. Alkylation proceeded with both regio- and diastereoselectivity, deprotonation and subsequent alkylation occurring predominantly on the less hindered side of the ketone functionality (opposite to the bridgehead methyl group). Alkylation occurred exclusively from the convex face of the bicyclic ring system (exo-alkylation), thus affording one diastereomer. No trace of any product resulting from endo-alkylation was ever detected by NMR or GC. The regioselectivity of the alkylation varied strongly with reaction conditions. Best results were obtained at low temperature with LDA as base, methyl iodide as alkylating agent and THF as solvent. Selectivities as high as 7:1 in favor of **6** could be obtained using these conditions. Initially, bis-alkylation appeared to be a problem, with a faster second alkylation occurring on the desired isomer, thus depleting the regioselectivity. It was found, however, that the presence of several equivalents of lithium chloride[20] suppressed bis-alkylation almost completely (<2%). After chromatographic separation from its regioisomer **7** and the doubly alkylated product **8**, **6** was afforded in modest yield.



Ketone **6** was transformed to the corresponding silyl enol ether **9** by treatment with LDA and chlorotrimethylsilane in THF. When run at -78 °C, this reaction proceeded in quantitative yield and with very high regioselectivity (>99:1) to afford **9**, which was used without purification. Ozonolysis of **9** followed by a reductive workup yielded a mixture of carboxylic acid **10** and hydroxy ketone **11**. This mixture was treated with sodium periodate in a water/THF mixture, cleaving hydroxy ketone **11** and affording **10** in 80% overall yield from **6**.



A Wittig olefination was employed to transform aldehyde **10** into the corresponding alkene **12**. Typically, two or more equivalents of base were used in the olefination because one equivalent of reagent was consumed in deprotonation of the acid functionality. Alkene **12** has been converted to davanone (**1**) by Birch *et al.*[5] by treatment with excess prenyllithium in the course of their synthesis. However, higher yields of **1** were obtained by conversion of **12** to the corresponding Weinreb amide **13**[21] and prenylation with prenylmagnesium chloride to provide **1** in 75% yield.



Conclusions

The total synthesis of the sesquiterpene (±)-davanone (**1**) has been completed successfully *via* a linear eight step sequence in 22% overall yield.

The Lewis acid catalyzed [3+4] annulation reaction of 1,4-pentanedione with bis-(trimethylsilyl) enol ether **2** was the key step in the synthesis, providing the means to selectively form the *cis*-disubstituted tetrahydrofuran ring moiety. The resulting oxabicyclo[3.2.1]heptanone system was selectively alkylated and elaborated further to provide (±)-davanone (**1**).

Experimental Section

General. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under Ar and then redistilled from sodium-benzophenone ketyl immediately prior to use. Methylene chloride (CH_2Cl_2) and diisopropylamine [$HN(i\text{-}Pr)_2$] were distilled from calcium hydride immediately prior to use. Pyridine was distilled from calcium hydride and stored under Ar. Iodomethane was distilled from magnesium sulfate ($MgSO_4$) and stored over copper turnings under argon. Trimethylsilyl chloride (TMSCl), thionyl chloride ($SOCl_2$) and trimethylsilyl triflate (TMSOTf) were distilled and stored under Ar. Lithium chloride (LiCl) was dried by recrystallizing in methanol followed by heating to 140 °C at 0.1 mm Hg overnight immediately prior to use. Other commercially available reagents were used without purification. Standard benchtop techniques were employed for handling air-sensitive reagents, and air-sensitive reactions were run under Ar in oven- or flame-dried glassware.

Methyl (5-Methyl-3-oxo-)-8-oxabicyclo[3.2.1]octane-2-carboxylate (**4**). A solution of 2.50 g (25.0 mmol) of 1,4-pentanedione and 7.80 g (30.0 mmol) of 1,3-bis(trimethylsiloxy)-1-methoxybuta-1,3-diene in 250 mL of CH_2Cl_2 was cooled to -50 °C and a solution of 556 mg (2.50 mmol) of TMSOTf in 10 mL CH_2Cl_2 was added over 1 h *via* cannula. The reaction was stirred for 12 h, warmed to rt and quenched with 100 mL of pH 7 buffer. The layers were separated and the aqueous layer was extracted with several portions of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel neutralized with 1% NEt_3 in hexanes using 10% EtOAc in hexanes as eluent to yield 4.55 g (92%) of the title compound as a colorless oil whose spectral characteristics were identical with the ones described in the literature.[11]

1-Methyl-8-oxabicyclo[3.2.1]oct-3-one (**5**). Keto ester **4** (1.00 g, 5.00 mmol) was dissolved in 40 mL of DMSO containing two drops of H_2O and 500 mg (11.9 mmol) of solid LiCl was added. The reaction mixture was heated at reflux for 2.5 h, quenched with 100 mL of brine and extracted with several portions of Et_2O. The Et_2O layers were washed with several portions of brine and the aqueous layers re-extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel with 10% Et_2O in light petroleum ether as eluent to yield

0.55 g (78%) of the title compound as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.67 ("appt" t, *J* = 6.1 Hz, 1H), 2.61 (dd, *J* = 15.3, 4.9 Hz, 1H), 2.44 (d, *J* = 15.3 Hz, 1H), 2.32 (d, *J* = 15.3 Hz, 1H), 2.22 (d, *J* = 15.3 Hz, 1H), 1.76-1.87 (m, 1H), 2.06-2.18 (m, 1H), 1.61-1.74 (m, 2H), 1.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.9, 81.3, 74.9, 55.1, 48.7, 35.7, 30.7, 26.2; **IR** (neat) 2970, 2881, 1719, 1378, 1263, 1195 cm^{-1}; **HRMS** calcd for $C_8H_{12}O_2$: 140.0837, found 140.0824; **LRMS** (EI^+) *m/z* 140 (100), 111(20), 82 (22), 55 (24), 43 (93).

[1R,4S*,5S*]-1,4-Dimethyl-8-oxabicyclo[3.2.1]oct-3-one* **(6).** A suspension of 403 mg (9.60 mmol) of dry LiCl in 5 mL of THF was stirred at -78 °C and 243 mg (2.40 mmol) of $HN(i\text{-}Pr)_2$ was added followed by 1.60 mL (2.60 mmol) of 1.6 M *n*-BuLi. The suspension was warmed to rt, re-cooled to -78 °C and a solution of 420 mg (3.00 mmol) of **5** in 10 mL THF was added slowly (over 2.5 h) *via* cannula. The reaction mixture was stirred for 4 h at -78 °C and a solution of 716 mg (5.00 mmol) of MeI in 5 mL THF was slowly added *via* cannula. The reaction was left to warm very slowly overnight, quenched with brine and extracted with several portions of Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel with 2% Et_2O and 10% CH_2Cl_2 in light petroleum ether as eluent to yield 268 mg (17.0 mmol, 58%; 73% yield based on recovered starting material) of the title compound as a colorless oil and 87 mg (0.60 mmol) of **5**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.29 (d, *J* = 7.4 Hz, 1H), 2.55 (dd, *J* = 15.4, 2.2 Hz, 1H), 2.10-2.24 (m, 3H), 1.72-1.80 (m, 1H), 1.56-1.69 (m, 2H), 1.41, (s, 3H), 1.22 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.1, 81.4, 79.9, 52.2, 51.9, 34.9, 30.5, 26.1, 16.5; **IR** (neat) 2972, 2879, 1716, 1455, 1379 cm^{-1}; **HRMS** calcd for $C_9H_{14}O_2$: 154.0994, found 154.0942; **LRMS** (EI^+) *m/z* 155 (98), 125 (79), 83 (50), 56 (50), 43 (100). Regioisomer **6** was isolated in 8% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.61 ("appt" t, *J* = 6.3 Hz, 1H), 2.74 (dd, *J* = 15.3, 5.4 Hz, 1H), 2.07-2.23 (m, 3H), 1.64-1.83 (m, 3H), 1.33 (s, 3H), 1.16 (d, *J* = 7.0 Hz, 3H) 1.19; **IR** (neat) 2974, 2881, 1717, 1412, 1328 cm^{-1}; **LRMS** (EI^+) *m/z* 154 (16), 83 (52), 82 (94), 56 (82), 43 (100). Doubly alkylated product **7** was isolated in 2% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.25 (d, *J* = 7.4 Hz, 1H), 2.10-2.23 (m, 3H), 1.64-1.77 (m, 3H), 1.33 (s, 3H), 1.26 (d, *J* = 7.8 Hz, 3H) 1.19 (d, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 216.6, 81.8, 79.9, 56.3, 51.5, 36.7, 30.9, 22.9, 18.0, 15.4; **IR** (neat) 2974, 1704, 1454, 1379, 1248 cm^{-1}; **HRMS** calcd for $C_9H_{14}O_2$: 168.1150, found 168.1145; **LRMS** (EI^+) *m/z* 168 (92), 125 (73), 86 (82), 83 (80), 43 (100).

[1R,4S*,5S*]-1,4-Dimethyl-3-trimethylsilyloxy-8-oxabicyclo[3.2.1]oct-2-ene* **(9).** LDA (2.50 mmol) was prepared by adding 1.56 mL (2.50 mmol) of 1.6 M *n*-BuLi to 304 mg (3.00 mmol) of $HN(i\text{-}Pr)_2$ in 4 mL of THF at 0 °C. The solution was cooled to -78 °C and a solution of 308 mg (2.00 mmol) of **6** in 10 mL THF was added slowly (over 2 h) *via* cannula. The reaction was stirred at -78 °C for 1 h, warmed to rt, re-cooled to -78 °C and a solution of 250 mg (2.30 mmol) of TMSCl in 5 mL of THF was added slowly *via* cannula. The reaction was warmed to rt, partly concentrated *in vacuo*, diluted with hexanes, filtered through Celite and concentrated *in vacuo*. The crude product (slightly yellow oil) was used without purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.80 (s, 1H), 4.18 (d, *J* = 10.2 Hz, 1H), 2.13 (q, *J* = 5.1 Hz, 1H),

1.92 (t, J = 9.2 Hz, 1H), 1.48-1.74 (m, 3H), 1.35 (s, 3H), 1.14 (d, J = 5.1 Hz, 3H), 0.17 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.8, 110.5, 79.4, 77.9, 43.3, 41.5, 30.6, 23.6, 17.5, 0.3.

[2α(R),5α]-5-Formyltetrahydro-α,5-dimethyl-2-furanacetic acid* **(10).** The crude product from above was dissolved in 10 mL of CH_2Cl_2 and cooled to -78 °C. Ozone was bubbled through the solution until a slightly blue color persisted. The reaction was poured into a suspension of 1.30 g (20.0 mmol) of zinc powder in 10 mL of 1 M HCl and stirred for 1 h. The layers were separated and the aqueous layer was extracted with several portions of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield a mixture of hydroxy ketone **11** and acid **10** with **11** as the major product (less than 10% of **10** by NMR integration). The crude mixture was dissolved in 8 mL of THF and 4 mL of H_2O and 1.07 g (5.00 mmol) of $NaIO_4$ was added. The reaction was stirred for 2 d at rt, quenched with 20 mL of 1 M HCl and the aqueous layer was extracted with several portions of Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography on silica gel with 10% EtOAc and 0.1% AcOH in hexanes as eluent to yield 372 mg (80% overall from **6**) of the title compound as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 4.26-4.33 (m, 1H), 2.46-2.58 (m, 1H), 2.21-2.30 (m, 1H), 2.04-2.14 (m, 1H), 1.67-1.77 (m, 1H), 1.51-1.61 (m, 1H), 1.28 (s, 3H), 1.14 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.9, 179.7, 87.2, 81.4, 45.2, 33.6, 29.6, 21.0, 13.3; **IR** (neat) 2977, 1732, 1712, 1460, 1379, 1205, 1106 cm^{-1}; **HRMS** calcd for $C_9H_{13}O_3$ ($M\text{-}OH^+$): 169.0865, found 169.0863; **LRMS** (EI^+) *m/z* 157 (85), 111 (78), 83 (38), 69 (69), 55 (34), 43 (100).

Hydroxy ketone **11** could be isolated by column chromatography on silica gel with 20% EtOAc and 0.1% AcOH in hexanes as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.24 (d, J = 7.0 Hz, 1H), 3.47 (brs, 1H), 2.82 (brs, 1H), 2.08-2.24 (m, 2H), 1.58-1.80 (m, 3H), 1.42 (s, 3H), 1.35 (d, J = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.3, 83.2, 80.4, 50.7, 32.3, 30.5, 21.0, 17.6; **IR** (neat) 3430 (broad), 2936, 1711, 1455, 1377, 1234, 1083 cm^{-1}; **LRMS** (EI^+) *m/z* 170 (13), 109 (19), 83 (32), 58 (31), 43 (100).

[2α(R),5α]-5-Ethenyltetrahydro-α,5-dimethyl-2-furanacetic acid* **(12).** A suspension of 322 mg (0.90 mmol) Ph_3PMeBr and 224 mg (2.00 mmol) of *t*-BuOK was stirred in 5 mL of THF at rt for 30 min. A solution of **10** in 10 mL of THF was added slowly *via* cannula and the reaction was stirred for 1 h, quenched with 10 mL of 1M HCl, and the aqueous layer extracted with several portions of Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography on silica gel with 20% EtOAc and 0.1% AcOH in hexanes as eluent to yield 127 mg (86%) of the title compound as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.88 (dd, J = 17.2, 10.6 Hz, 1H), 5.21 (dd, J = 17.2, 1.2 Hz, 1H), 4.99 (dd, J = 10.6, 1.2 Hz, 1H), 4.12-4.19 (m, 1H), 2.51-2.56 (m, 1H), 2.01-2.08 (m, 1H), 1.90-1.97 (m, 1H), 1.76-1.82 (m, 1H), 1.59-1.75 (m, 1H), 1.31 (s, 3H), 1.12 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.6, 143.8, 112.1, 84.0, 80.3, 45.3, 37.6, 29.8, 26.5, 13.2; **IR** (neat) 2975, 2940, 1711, 1370, 1250, 1029 cm^{-1}; **HRMS** calcd

for $C_9H_{13}O_3$ ($M\text{-}CH_3^+$): 169.0865, found 169.0871; **LRMS** (EI^+) *m/z* 169 (41), 111 (35), 69 (33), 55 (100), 43 (26).

[2α(R),5α]-2-(5-Ethenyltetrahydro-5-methyl-2-furanyl)-N-methoxy-N-methyl-propanamide* **(13).** 60 mg (0.33 mmol) of **12** were dissolved in 0.50 mL of $SOCl_2$ and stirred at rt for 1 h. The $SOCl_2$ was removed *in vacuo* and the resultant acid chloride was dissolved in 5 mL of CH_2Cl_2 and 49 mg (0.50 mmol) of solid *N,N*-dimethyl hydroxylamine hydrochloride was added. The solution was cooled to 0 °C and 79 mg (1.00 mmol) of pyridine was added. The reaction was stirred at rt for 1 h, quenched with 10 mL of brine, and the aqueous layer was extracted with several portions of Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography on silica gel with 15% EtOAc in light petroleum ether as eluent to yield 61 mg (82%) of the title compound as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.88 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.15 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.92 (dd, *J* = 10.6, 1.6 Hz, 1H), 4.12-4.26 (m, 1H), 3.69 (s, 3H), 3.18 (s, 3H), 2.92-3.08 (brm, 1H), 1.94-2.03 (m, 1H), 1.84-1.92 (m, 1H), 1.70-1.79 (m, 1H), 1.60-1.69 (m, 1H), 1.26 (s, 3H), 1.03 (d, *J* = 7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.8, 111.2, 82.7, 80.2, 61.5, 40.9, 37.7, 29.2, 26.4, 13.6; **IR** (neat) 2968, 1661, 1652, 1464, 1418, 1386 cm^{-1}; **HRMS** calcd for $C_{12}H_{21}O_3N$: 227.1512, found 227.1511; **LRMS** (EI^+) *m/z* 167 (25), 111 (100), 93 (73), 69 (38), 55 (42), 41 (43).

[2α(R),5α]-2-(5-Ethenyltetrahydro-5-methyl-2-furanyl)-6-methyl-5-hepten-3-one* **(1).** 61 mg (0.27 mmol) of **(10)** in 10 mL THF were stirred at rt and 0.30 mmol (0.60 mL of a 0.5 M solution) of prenylmagnesium chloride (freshly prepared from 1-chloro-3-methyl-2-butene and magnesium powder in THF) was added. The reaction was stirred for 1 h, quenched with 10 mL of brine, and the aqueous layer was extracted with several portions of Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by column chromatography on silica gel with 20% Et_2O in light petroleum ether as eluent to yield 48 mg (75%) of the title compound as a colorless oil whose spectral characteristics were identical with the ones described in the literature.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.88 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.28-5.36 (m, 1H), 5.17 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.96 (dd, *J* = 10.6, 1.6 Hz, 1H), 4.02-4.11 (m, 1H), 3.16-3.34 (m, 2H), 2.62-2.74 (m, 1H), 1.92-2.02 (m, 1H), 1.83-1.91 (m, 1H), 1.66-1.77 (m, 1H), with overlapping s at 1.73 (3H), 1.50-1.64 (m, 1H), with overlapping s at 1.59 (3H), 1.23 (s, 3H), 0.97 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.1, 144.7, 135.4, 116.0, 111.3, 83.0, 81.0, 51.2, 42.7, 37.5, 29.8, 26.6, 25.7, 18.0, 13.1; **IR** (neat) 2971, 2928, 1716, 1456, 1374, 1100, 1028 cm^{-1}; **LRMS** (EI^+) *m/z* 236 (6), 111(100), 93 (53), 69 (66), 55 (40), 41 (65).

Acknowledgments

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References

1. Misra L; Chandra A; Thakur R. *Phytochemistry* **1991**, *30*, 549-552 and references therein.
2. Hethelyi E; Tetenyi P; Kettenes-van der Bosch J; Salemink C; Heerma W; Verluis C; Kloosterman J; Sipma G. *Phytochemistry* **1981**, *20*, 1847-1850.
3. Sipma G; van der Wal B. *Recl. Trav. Chim. Pay. B.* **1968**, *87*, 715.
4. Naegeli P; Weber G. *Tetrahedron Lett.* **1970**, 959-962.
5. Birch A; Corrie J; Rao G. *Aust. J. Chem.* **1970**, *23*, 1811.
6. Ohloff G; Giersch W. *Helv. Chim. Acta* **1970**, *53*, 841-843.
7. Honda Y; Ori A; Tsuchihashi G. *Chem. Lett.* **1987**, 1259-1262 and references therein.
8. Bartlett P; Holmes C. *Tetrahedron Lett.* **1983**, *24*, 1365-1368.
9. Molander G; Andrews S. *Tetrahedron Lett.* **1989**, *30*, 2351-2354.
10. Molander G; Cameron K. *J. Org. Chem.* **1991**, *56*, 2617-2619.
11. Molander G; Cameron K. *J. Am. Chem. Soc.* **1993**, *115*, 830-848.
12. Molander G; Siedem C. *J. Org. Chem.* **1995**, *60*, 130-138.
13. Molander G; Eastwood P. *J. Org. Chem.* **1995**, *60*, 8382-8393.
14. Molander G; Eastwood P. *J. Org. Chem.* **1996**, *61*, 1910-1911.
15. Molander G; Swallow S. *J. Org. Chem.* **1994**, *59*, 7148-7151.
16. Molander G; Eastwood P. *J. Org. Chem.* **1995**, *60*, 4559-4565.
17. Molander G; Carey J. *J. Org. Chem.* **1995**, *60*, 4845-4849.
18. Krapcho P. *Synthesis* **1982**, 805-822.
19. Krapcho P. *Synthesis* **1982**, 893-914.
20. Hall P; Gilchrist J; Collum D. *J. Am. Chem. Soc.* **1991**, *113*, 9571-9574.
21. Nahm S; Weinreb S. *Tetrahedron Lett.* **1981**, *22*, 3815-3818.