Reaction of (1*S*,6*S*)-1,7,7-Trimethyl-2,3-dimethylene-*trans*-bicyclo[4.4.0]decane with Thallium(III) Acetate; a New Route to (−)-Warburganal and (+)-Euryfuran

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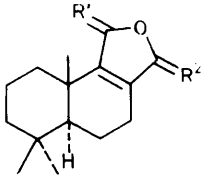
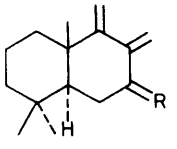
Oxidation of the diene (**2a**), obtainable in two steps from manool, with thallium(III) acetate in acetic acid yielded five products. After alkaline hydrolysis they were shown on the basis of spectroscopic evidence to be (**2b**), (**3a**), (**4**), (**5a**), and (**6a**). These compounds may be considered as useful intermediates to naturally occurring drimanes. On oxidation with pyridinium dichromate compound (**3a**) afforded the aldehyde (**3b**), whose acetal (**3c**) had previously been employed in the synthesis of warburganal (**7a**). Oxidation of compound (**4**) with pyridinium chlorochromate yielded in one step the (+)-form (**8**) of euryfuran.

A variety of synthetic routes[1] to drimane sesquiterpenes have appeared in recent years because of the intriguing biological properties of the latter. Earlier we published details of convenient and highly efficient syntheses of two naturally occurring members of this class, (+)-confertifolin[2] (**1a**) and (+)-isodrimenin[3] (**1b**). In these syntheses, (1*S*,6*S*)-1,7,7-trimethyl-2,3-dimethylene-*trans*-bicyclo[4.4.0]decane (**2a**),



(**1**) **a**; R' = H_2, R_2 = O
b; R' = O, R^2 = H_2



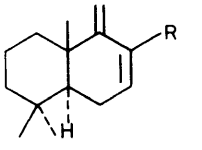
(**2**) **a**; R = H_2
b; R = =C(OH)H

obtainable (47% yield) in two steps from manool, served as a common, extremely useful intermediate. In the present work we demonstrate how it can also be used as a precursor for other related natural drimanes.

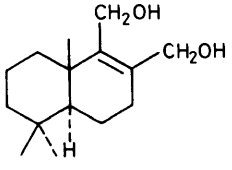
Results and Discussion

Recent interesting reports[4,5] on the oxidation of some conjugated dienes by thallium(III) salts persuaded us to investigate the behaviour of the diene (**2a**) on thallium(III) acetate oxidation.

When the diene (**2a**) was treated with this reagent in acetic acid containing 5% acetic anhydride, a rather complex mixture of products was obtained. We first divided this mixture of acetates into two major fractions A and B by chromatographic separation on silica gel. The fraction A (36% yield) which consisted of two compounds, as demonstrated by t.l.c., was obtained by elution with 2% ether in hexane, and was found to be a mixture of olefinic mono-acetate derivatives by a combination of ^{1}H n.m.r. and mass spectroscopic evidence. It was hydrolysed with 15% potassium carbonate in methanol at room temperature and a mixture of the resulting alcohols was subjected to chromatography over silica gel. The first product (45% yield) was eluted with 8% ether in hexane and formulated on the basis of the ^{1}H n.m.r. spectrum as (**2b**), $C_{15}H_{24}O$. In the spectrum a pair of 2 H multiplets, characteristic of the original diene system, was observed at δ 4.80 and 4.98. A 1 H multiplet at δ 4.43 ($W_{\frac{1}{2}}$, 8 Hz) was taken as evidence for the presence of an α-oriented (axial) secondary hydroxy group at C-7. The second product (40% yield), which was eluted with 12% ether in hexane, was found to be (**3a**). It has the same molecular formula as the above alcohol, but the presence of a primary hydroxy group, associated with the $\Delta^{7,8}$-double bond, was clearly shown by the signals of a 2 H singlet at δ 4.26 and a 1 H multiplet at δ 5.93 in the ^{1}H n.m.r. spectrum. A further 2 H broad singlet at δ 4.93 was assigned to the exocyclic double bond at C-9.



(**3**) **a**; R = CH_2OH
b; R = CHO
c; R = $HC(OCH_2CH_2CH_2O)$



(**4**)

Fraction B (49% yield), which was eluted with 10% ether in hexane, comprised a mixture of three different olefinic diacetate derivatives. After having been hydrolysed in a similar way as for the fraction A, the mixture was chromatographed over silica gel using hexane–ether as a solvent system. The most polar product (35% yield) was found to be the diol (**4**), $C_{15}H_{26}O_2$. In its ^{1}H n.m.r. spectrum two primary hydroxy groups resonated as a pair of a 2 H quartet (AB system) at δ 4.08 (*J* 11 Hz) and δ 4.16 (*J* 12 Hz), but no olefinic proton was detected. The second and third products, similar in polarity but less polar than the first, have identical molecular formulae ($C_{15}H_{26}O_2$). The one (17% yield) of slightly less polarity had m.p. 127—128 °C, and the other (30% yield), had m.p. 70—72 °C. These diols were presumed to result from the reaction of only one of the two exocyclic double bonds in (**2a**) with thallium(III) acetate. Their ^{1}H n.m.r. spectra revealed that an exocyclic double bond [in the diol, m.p. 127—128 °C, δ 4.74 (1 H, br s) and 4.97 (1 H, br s); in the diol, m.p. 70—72 °C, δ 5.03 (2 H, m)] and a primary hydroxy group [in the diol, m.p. 127—128 °C, δ 3.88 (2 H, AB system, *J* 11 Hz); in the diol, m.p. 70—72 °C, δ 3.83 (2 H, AB system, *J* 11 Hz)] were present, but they lacked a secondary hydroxy function; this suggested that one of the two hydroxy groups in these diols is tertiary. This agreed with the observation that both compounds afforded a mono-acetate under ordinary acetylating conditions. Furthermore, the spectra showed signals

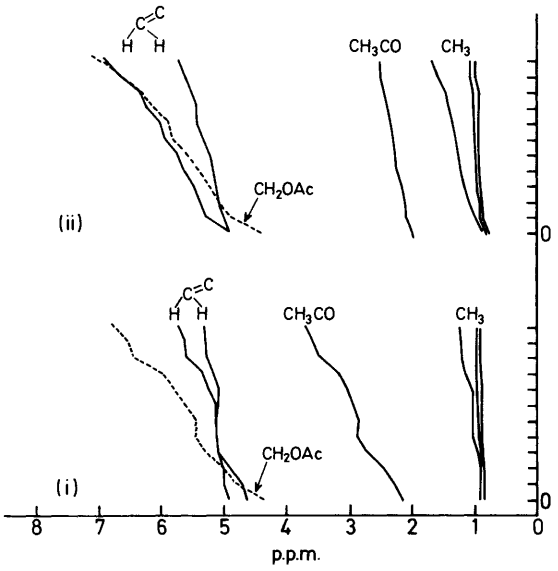
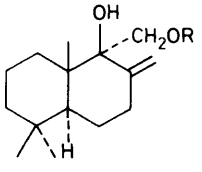
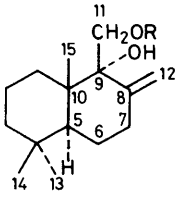


Figure. ^{1}H N.m.r. spectra of (i) the mono-acetate B (**5b**) and (ii) the mono-acetate A (**6b**) upon addition of Eu([$^2H_6$]fod)

for allylic protons at δ 2.55 (2 H, m, in the diol, m.p. 127—128 °C) and δ 2.48 (2 H, m, in the diol, m.p. 70—72 °C); hence both diols must possess an exocyclic double bond at C-8 (not at C-9). It is thus evident that one of these two alcohols possesses structure (**5a**) and the other, structure (**6a**), *viz.* the difference



(**5**) **a**; R = H
b; R = Ac



(**6**) **a**; R = H
b; R = Ac

between them resides in the stereochemistry at C-9. In order to differentiate these two isomeric structures (**5a**) and (**6a**), we have studied the n.m.r. spectroscopic behaviour of the mono-acetates A and B in the presence of a shift reagent.[6] The spectra of these two compounds at varying ratios of Eu([$^2H_6$]fod)$_3$ are shown in the Figure. In both cases preferential complexation of the shift reagent at the ester rather than at the tertiary hydroxy group was observed. In the spectrum of the monoacetate B, although the resonances due to the ester function suffered large downfield chemical shifts, both the exocyclic methylene and the angular methyl protons experienced only small induced effects; this indicated that the co-ordination took place predominantly at the α-oriented ester group in structure (**5b**), in which it is remote from the latter groups. The spatial congestion of the tertiary hydroxy group* in (**5b**), due to both the adjacent exocyclic double bond and the angular methyl group at C-10 may account for the predominance of the association of the lanthanide with this ester site. In the spectrum of the mono-acetate A, however, both signals for the exocyclic double bond and one of the angular methyl groups were markedly affected, and their induced chemical shifts were found to be parallel to those of the ester group. This pointed to structure (**6b**) for the mono-acetate A, in which the methyl at C-10 and the ester group are on the same β-side. We therefore formulated the mono-acetates A and B, and the diol, m.p. 70—72 °C and the diol, m.p. 127—128 °C as (**6b**) and (**5b**), and (**6a**) and (**5a**), respectively.

This structure assignment was also confirmed by ^{13}C n.m.r. spectroscopy. Complete assignments of the signals of the monoacetates A (**6b**) and B (**5b**) were made by the gated decoupled spectra based on the data reported for manool and its related compounds[7] (see the Experimental section). The monoacetates A and B showed a very sharp triplet of triplets for the signals at δ 108.2 [in (**6b**)] and δ 109.8 [in (**5b**)] due to the exocyclic olefinic carbon-12. This coupling pattern results from the splittings caused by the two geminal vinyl hydrogens (J_{CH} 155 Hz) and the two allylic hydrogens (J_{CCH} 6 Hz) at C-7. If manool and its related compounds, with a β-side chain at C-9, are taken as model compounds, the magnitudes of the γ-substituent effects of the hydroxy group on C-1, C-5, C-7, and C-15 (−6.1, −6.5 ± 0.1, −5.4 ± 0.1, and 0.4 p.p.m., respectively), are compatible with the stereochemistry shown for compound (**6b**). It has recently been reported[8] that in similar bicyclic ring compounds possessing an α-alkyl substituent at C-9, the C-15 angular methyl carbon resonates at δ 21—23.† It is interesting to note that in compound (**5b**) the same 15-methyl resonance is shifted upfield to δ 16.7. This may be due to a large shielding γ-effect caused by additional introduction of a β-hydroxy function at C-9.

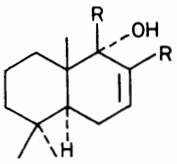
Having determined the structures of the above five products (**2a**), (**3a**), (**4**), (**5a**), and (**6a**), it appeared to be attractive to investigate their possible use as precursors to naturally occurring drimanes. We considered compound (**3a**) as a good candidate to (−)-warburganal (**7a**). Oxidation with pyridinium dichromate[9] provided in 67% yield the aldehyde (**3b**). Subsequent refluxing of (**3b**) with propane-1,3-diol in benzene in the presence of toluene-*p*-sulphonic acid led in 51% yield to the acetal (**3c**) which has previously been synthesized in racemic form *via* a different route.[10] Since this compound has already been converted[10] into warburganal, our present approach constitutes a formal route to (−)-warburganal‡ (**7a**) from manool.

The furanosesquiterpene (**8**) has recently been obtained in (−)-form from the nudibranches[11] *Hysselodoris californiensis* and *H. porterae*, and in (+)-form from the sponges *Dysidea herbacea*[12] and *Euryspongia* species,[11] but its absolute stereochemistry was undetermined. At the same time[2] when we first synthesized this compound, it had not yet been encountered in Nature, and the absolute configuration of the natural substance, therefore, still remained to be determined. We have previously shown that on treatment with basic alumina or other appropriate reagents, the endoperoxide[2] (**9**), obtained by the photo-oxygenation of the diene (**2a**), yielded in one step an euryfuran (**8**) (*via* rearrangement to an intermediate lactol, followed by dehydration). Nishiyama *et al.*[13] recently reported that (*Z*)-but-2-ene-1,4-diols could be converted, with pyridinium chlorochromate, into furans by a one-step oxidation–dehydration process involving lactols as intermediates. Application of this latter procedure to the diol (**4**)

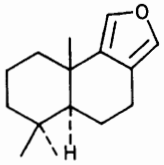
* This equatorially oriented C–O bond is nearly eclipsed by the exocyclic double bond.

† Note that those compounds which bear a β-alkyl substituent at C-9 show a corresponding methyl resonance at δ 14—15.

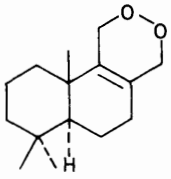
‡ For the syntheses of optically active dimanic sesquiterpenes, see E. Wenkert and D. P. Strike, *J. Am. Chem. Soc.*, 1964, **86**, 2044; H. Okawara, H. Nakai, and M. Ohno, *Tetrahedron Lett.*, 1982, **23**, 1087; M. L. Oyarzún, M. Cortés, and J. Sierra, *Synth. Commun.*, 1982, 955; M. J. Cortés, I. Razmilic, J. R. Sierra, and J. López, *Chem. Ind. (London)*, 1985, 735; S. V. Ley, in 'Recent Advances in the Chemistry of Insect Central,' Special Publication, Royal Society of Chemistry, 1985, no. 53, p. 307; K. Mori and H. Watanabe, *Tetrahedron*, 1986, **42**, 273.



(7) **a**; R = CHO
b; R = CH_2OH



(8)



(9)

afforded in 72% yield an euryfuran, which showed $[\alpha]_D$ +19° ($CHCl_3$), thereby establishing the absolute configuration (**8**)* for the (+)-form of the natural substance.†

Finally, we attempted to convert compound (**6a**) into compound (**7b**), a direct precursor to (−)-warburganal (**7a**). For this purpose photo-oxygenation seemed to be a method of choice. However, compound (**6b**) was found to be very resistant to this oxygenation, and we could not, therefore, proceed further.

Experimental

M.p.s were taken with a Kofler hot-stage apparatus and are uncorrected. Unless otherwise specified, i.r. spectra were recorded on a Perkin-Elmer 577 spectrometer as neat oils and ^1H and ^{13}C n.m.r. spectra were determined for solutions in $CDCl_3$ with $SiMe_4$ as internal standards using a Varian EM-3940 spectrometer and a Bruker WP-80 spectrometer operating in the Fourier transform mode, respectively. Mass spectra were recorded with a DuPont 21-492B mass spectrometer at 70 eV using a direct inlet system. Rotations were measured at 23—25 °C with a Zeiss '0.01°' polarimeter for solutions in $CHCl_3$. For column chromatography Merck silica gel (70—230 mesh ASTM) was used. Thin layer chromatograms were prepared on Merck silica gel 60 GF_{254} and the spots were observed either by exposure to iodine vapour or by u.v. light. All organic extracts were dried over anhydrous sodium sulphate and evaporated under reduced pressure below 60 °C.

Oxidation of the Diene (**2a**) *with Thallium*(III) *Acetate*.—A solution of the diene (**2a**) (1.272 g, 6.24 mmol) in a mixture (50 ml) of glacial acetic acid–acetic anhydride (95:5) was stirred with thallium(III) acetate (1.696 g, 5.17 mmol) at room temperature for 18 h, then at 45 °C for 7 h, and finally at room temperature for 17 h. The reaction mixture was diluted with water and extracted with ether. The ether extract was washed with water, dried, and evaporated. The crude product was then chromatographed over silica gel. Unchanged diene (**2a**) (145 mg, 11%) was recovered by elution with hexane. Elution with 2% ether in hexane yielded the fraction A (519 mg, 35.8%), which was a mixture of two compounds as demonstrated by t.l.c. This fraction apparently consisted of olefinic mono-acetate derivatives since the ^1H n.m.r. spectrum showed signals for acetate groups and olefinic protons while in the mass spectrum only a single molecular ion peak was observed at *m/z* 262. Elution with 10% ether in hexane afforded the fraction B (867 mg, 48.8%) which was a mixture of two compounds (t.l.c.). The ^1H n.m.r. spectrum also contained signals for acetate groups and olefinic protons, but it gave a molecular ion peak at *m/z* 322, indicating that it was composed of olefinic di-acetate derivatives.

Hydrolysis of Fraction A *and Isolation of the Alcohols* (**2b**) *and* (**3a**).—Fraction A (519 mg) was treated with a suspension of potassium carbonate (4.5 g) in methanol (30 ml) at room temperature for 4 h. Water was added, and the product was extracted with ether and then chromatographed over silica gel. Elution with 8% ether in hexane yielded the *alcohol* (**2b**) (194 mg) as an oil; δ_H (90 MHz) 0.88, 0.90, and 0.96 (3 H, each, s, CH_3), 4.43 (1 H, m, $W_{\frac{1}{2}}$ 8 Hz, C*H*OH), 4.80 (2 H, m, C=CH_2), and 4.98 (2 H, m, C=CH_2); *m/z* 220 (M^+), 205, 202, 189, and 187 (Found: C, 81.4; H, 10.7. $C_{15}H_{24}O$ requires C, 81.76; H, 10.98%). Elution with 12% ether in hexane afforded the *alcohol* (**3a**) (172 mg) as an oil; δ_H (90 MHz) 0.86, 0.91, and 0.96 (3 H, each, s, CH_3), 2.15 (2 H, m, allylic H), 4.26 (2 H, br s, C=CH_2), 4.93 (2 H, br s, CH_2OH), and 5.93 (1 H, m, CH=C); *m/z* 220 (M^+), 205, 202, 189, and 187 (Found: C, 81.55; H, 10.75. $C_{15}H_{24}O$ requires C, 81.76; H, 10.98%).

Hydrolysis of Fraction B *and Isolation of the Alcohols* (**4**), (**5a**), *and* (**6a**).—Fraction B (1.218 g) was hydrolysed in the same way as for fraction A. The crude product was chromatographed over silica gel using hexane–ether as a solvent system. The *alcohol* (**5a**) (153 mg) was obtained from the least-polar fraction and showed m.p. 127—128 °C; $\nu_{max.}$(KBr) 3 375 (OH) and 1 645 cm^{-1} (exocyclic C=C); *m/z* 238 (M^+), 223, 220, and 207; δ_H (90 MHz) 0.86 (6 H, s, 2 × CH_3), 0.93 (3 H, s, CH_3), 2.55 (2 H, m, allylic protons), 3.88 (2 H, AB q, *J* 11 Hz, CH_2OH), 4.74 (1 H, m), and 4.97 (1 H, m, C=CH_2) (Found: C, 75.25; H, 10.65. $C_{15}H_{26}O_2$ requires C, 75.58; H, 11.00%).

The *alcohol* (**6a**) (269 mg) was slightly more polar than the alcohol (**5a**), and had m.p. 70—72 °C; $\nu_{max.}$(KBr) 3 400 (OH) and 1 640 cm^{-1} (exocyclic C=C); *m/z* 238 (M^+), 223, 220, and 207; δ_H (90 MHz) 0.86, 0.90, 0.93 (3 H, each, s, CH_3), 2.48 (2 H, m, allylic H), 3.83 (2 H, AB q, *J* 11 Hz, CH_2OH), and 5.03 (2 H, m, C=CH_2) (Found: C, 75.35; H, 10.75. $C_{15}H_{26}O_2$ requires C, 75.58; H, 11.00%).

The most-polar fraction contained the *alcohol* (**4**) (313 mg), m.p. 128—130 °C; $\nu_{max.}$(KBr) 3 370 cm^{-1} (OH); *m/z* 238 (M^+), 223, 220, and 207, δ_H (90 MHz) 0.86, 0.90, and 1.00 (3 H, each, s, CH_3), 2.40 (2 H, m, allylic H), 4.08 (2 H, AB q, *J* 11 Hz, CH_2OH), and 4.16 (2 H, AB q, *J* 12 Hz, CH_2OH) (Found: C, 75.4; H, 10.85. $C_{15}H_{26}O_2$ requires C, 75.58; H, 11.0%).

Acetylation of the Alcohols (**6a**) *and* (**5a**).—The alcohol (**6a**) (110 mg) was treated with pyridine–acetic anhydride (3:1; 5 ml) at room temperature overnight. Work-up yielded the mono-acetate (**6b**) as an oil (105 mg); δ_H (90 MHz) 0.83, 0.87, and 0.90 (3 H, each, s, CH_3), 1.96 (3 H, s, Ac), 2.39 (2 H, m, allylic H), 4.45 (2 H, AB q, *J* 11 Hz, CH_2OAc), and 4.90 (2 H, m, C=CH_2); δ_C (21.1 MHz) 14.8 (C-15), 18.9 (C-2), 20.9 (CH_3CO), 22.4 (C-14), 23.2 (C-6), 32.8 (C-7 or C-1), 32.9 (C-1 or C-7), 33.7 (C-4), 34.0 (C-13), 42.2 (C-3), 43.0 (C-10), 48.9 (C-5), 66.9 (C-11), 79.9 (C-9), 108.2 (C-12), 148.8 (C-8), and 171.7 ($COCH_3$) (Found: C, 72.55; H, 9.7. $C_{17}H_{28}O_3$ requires C, 72.82; H, 10.06%).

Acetylation of the alcohol (**5a**) (98 mg) in the same way as above afforded the mono-acetate (**5b**) as an oil (100 mg); δ_H (90 MHz) 0.83, 0.87, and 0.90 (3 H each, s, CH_3), 2.06 (3 H, s, Ac), 2.49 (2 H, m, allylic H), 4.35 (2 H, AB q, *J* 12 Hz, CH_2OAc), and 4.60 and 4.91 (1 H each, br s, C=CH_2); δ_C (21.1 MHz) 16.7 (C-15), 19.1 (C-2), 21.1 (CH_3CO), 22.1 (C-14), 23.6 (C-6), 32.4 (C-7 or C-1), 33.1 (C-1 or C-7), 33.5 (C-4), 33.9 (C-13), 41.6

* It should be noted that all the formulae depicted in the drawings represent correct absolute configurations since they were derived from manool with known absolute stereochemistry.

† The work also established that (−)-euryfuran (Faulkner) should be drawn as the antipode of (+)-(**8**).

(C-3), 42.4 (C-10), 45.1 (C-5), 78.0 (C-9), 64.9 (C-11), 109.8 (C-12), 148.4 (C-8), and 171.2 ($COCH_3$) (Found: C, 72.6; H, 9.85. $C_{17}H_{28}O_3$ requires C, 72.82; H, 10.06%).

Oxidation of the Alcohol (**3a**) *with Pyridinium Dichromate.*—The alcohol (**3a**) (286 mg, 1.30 mmol) in methylene dichloride (3 ml) was treated with pyridinium dichromate (696 mg, 1.96 mmol) at room temperature for 20 h. After dilution with ether, the reaction mixture was filtered through silica gel and the filtrate was evaporated to yield the *aldehyde* (**3b**) (186 mg, 67%) as an oil; $\nu_{max.}$ 1 690 cm^{-1} (CHO); δ_H (90 MHz) 0.90, 0.93, and 0.95 (3 H each, s, CH_3), 2.39 (2 H, m, allylic H), 5.15 (1 H, br s), 5.93 (1 H, br s, C=CH_2), 6.73 (1 H, m, C=CH), and 9.60 (1 H, s, CHO) (Found: C, 82.25; H, 10.45. $C_{15}H_{22}O$ requires C, 82.51; H, 10.16%).

Acetalization of the Aldehyde (**3b**).—The aldehyde (**3b**) (186 mg) in benzene (20 ml) was heated under reflux with a water separator in the presence of toluene-*p*-sulphonic acid (5 mg) for 21 h. The solution was then washed with aqueous sodium hydrogen carbonate, dried, and evaporated. The crude product was filtered in hexane–ether through silica gel to yield the acetal (**3c**) (120 mg, 51%) as an oil; δ_H (90 MHz) 0.83, 0.91, and 0.96 (3 H each, s, CH_3), 2.18 (2 H, m, allylic H), 4.00 (6 H, m, $OCH_2CH_2CH_2O$) 4.95 (1 H, br s, OCHO), 5.08 (2 H, d, *J* 1.5 Hz, C=CH_2), and 6.26 (1 H, m, C=CH) (Found: C, 77.85; H, 9.85. $C_{18}H_{28}O_2$ requires C, 78.21; H, 10.21%).

Oxidation of the Alcohol (**4**) *with Pyridinium Chlorochromate.*—The alcohol (**4**) (233 mg, 0.89 mmol) in methylene dichloride (5 ml) was treated with pyridinium chlorochromate (531 mg, 1.53 mmol) at room temperature for 25 min. The reaction mixture was filtered through silica gel and the filtrate was evaporated. Chromatography of the resulting crude product in hexane–ether over silica gel yielded euryfuran (**8**) (155 mg, 72%) as an oil, identical with that synthesized previously;[2] $[\alpha]_D$ +19° (*c* 1.0); δ_H (90 MHz) 0.90, 0.94, and 1.18 (3 H each s, CH_3), 2.2—2.9 (2 H, m, allylic H), and 6.95 (2 H, br s, furan H).

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