Chemistry of Natural Compounds and Bioorganic Chemistry

Synthesis and structure of tricyclic furanosesquiterpenoids related to pallescensin A

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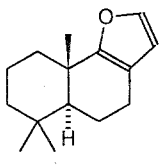
Electrophilic cyclization of (cyclo)farnesanes containing an *exo*-methylene group in the α-isoprenoid unit smoothly gives regio- and stereoisomeric octalins subsequently transformed to tricyclic furanosesquiterpenoids related to metabolites of some marine organisms.

Key words: furanosesquiterpenoids, pallescensin A, (cyclo)farnesanes, electrophilic cyclization; ^{1}H and ^{13}C NMR spectra, z-HMQC; molecular mechanics, conformational analysis.

In a continuation of the search for efficient routes for constructing the molecules of natural furanodecalins from acyclic precursors (*cf.* Ref. 1), this communication deals with the synthesis of some isomers of the metabolite of *Dysidea* marine fungus, pallescensin A (**1**),[2b,3] the structure of which has been established by spectral data[2b] and by complete[4—8] or partial[2b,9,10] syntheses, including the biomimetic cyclization of pallescensin-1 (**2**).[2b,9]



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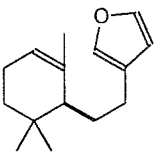

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† Deceased.

The strategy chosen by us for approaching the target furanosesquiterpenoids includes obtaining the appropriate linear or monocyclic farnesane derivatives at the first synthesis stage followed by their transformation by electrophilic cyclization (EC) to give intermediate decalins. Skeleton functionalization of the latter ensures the formation of the lacking annelated furan fragment at the final stage. Using this approach, the respective starting homoallylic alcohols **4** and **5** of the (cyclo)farnesane series were prepared in high yields from isobutenylcarbinol (**3**), geranyl- or neryl chloride, and α-cyclogeranyl bromide under the conditions similar to those reported in Ref. 11 (Scheme 1). The structures of trienol *Z*-**4** insufficiently characterized previously[12] and the hitherto unknown dienol **5** were established on the basis of elemental analysis data, IR and mass spectra, as well as ^{1}H and ^{13}C NMR data for these compounds. The

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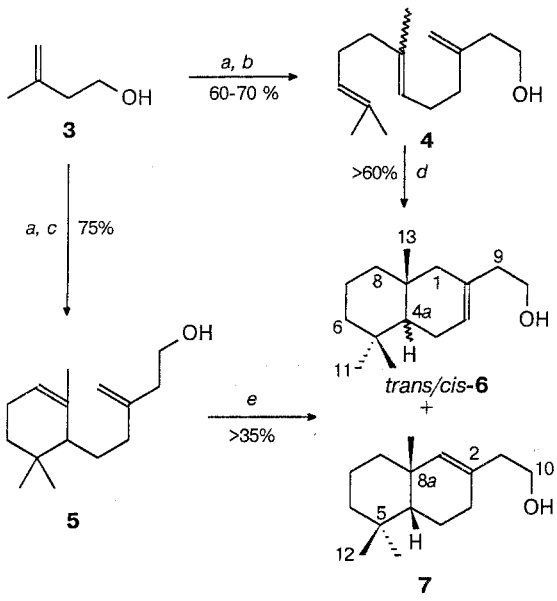
Scheme 1



Reagents and conditions: *a*, *n*-BuLi/hexane/TMEDA, 25 °C; *b*, geranyl or neryl chloride/THF, −70→25 °C; *c*, α-cyclogeranyl bromide/THF, −70→25 °C; *d*, $F_3B \cdot OEt_2$/hexane, 0→25 °C; *e*, $F_3B \cdot OEt_2/CH_2Cl_2$, 0→25 °C.

structure of the known[11] alcohol *E*-**4** was confirmed by spectral data.

A search for the conditions of efficient EC of sesquiterpenic trienes **4** revealed that the use of an emulsion of the substrate and ~3 mol-eq. $F_3B \cdot OEt_2$ in hexane at 0 °C are the optimum conditions. Under these conditions, triene *E*-**4** is transformed in high yield into a mixture of octalins **6** with a ≈5:1 ratio of *trans* and *cis* isomers (Scheme 1). Under the same conditions, the *Z*-**4** isomer equally efficiently gives rise to a mixture of olefins **6** with an almost reverse ratio of C(4*a*) epimers, *cis*/*trans* ≈ 6:1. Simultaneously, the *cis* regioisomer **7** is formed, whose relative content in the reaction mixture reaches 20 % for *Z*-**4** but does not exceed 3 % in the products of *E*-**4** cyclization.

It turned out that the optimum conditions for the EC of diene **5** consist in the use of 2.3 mol-eq. of $F_3B \cdot OEt_2$ in CH_2Cl_2 at 0 °C. This reaction gives a mixture of the above octalins as the main reaction products, *cis*-**6**/*trans*-**6**/**7** ratio ≈ 3 : 1 : 1 (^{1}H NMR and HPLC data), in a moderate yield.

The observed high *trans*-stereoselectivity for EC of triolefin *E*-**4** and *cis*-selectivity for EC of triene *Z*-**4** or α-cyclofarnesadiene **5**, which possess an exomethylene terminator in all cases, is consistent with the known stereochemical consequence of this reaction in the series of linear and monocyclic oligoolefins[13–18] and with the results of the Lewis acid-initiated cyclization of the furans, dendrolasine and pallescensin **2**, which are related to homoallylic alcohols *E*-**4** and **5**, to give predominantly compound (±)-*trans*-**1** [4] or its chiral *cis*-C(4*a*) epimer,[9] respectively. The simultaneously found relatively low content of regioisomer **7** indicates the high degree of synchronism of the EC of substrates **4** and **5** terminated by the disubstituted C=C bond.

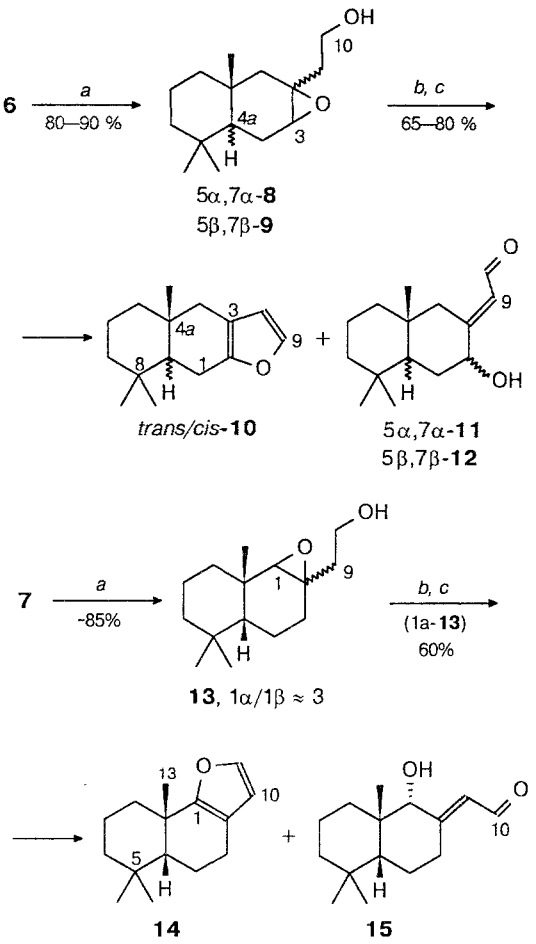
The structures of the hitherto unknown octalins **6** and **7** isolated in the individual state by HPLC was established on the basis of elemental analysis and spectral data for these compounds. The position of the double bond in compounds **6** and **7** follows from the multiplicity revealed in their ^{1}H NMR spectra for four and two allylic protons in cycle *B*. The same is confirmed by the marked nuclear Overhauser effect (NOE) for $H_3C(13)$ and HC(1) protons, one of the allylic protons for olefins **6**, or the vinyl proton for their regioisomer **7**. The same method reveals the spatial proximity of one of the allyl $H_2C(3)$ protons with methyl $H_3C(11)$ protons, which is possible only in the case of *cis*-*A*/*B* coupling in this molecule. Similarly, the differential NOE spectrum of octalin *cis*-**6** demonstrates the interaction of adjacent HC(4*a*) and $H_3C(13)$ protons. This effect is not observed in the case of the *trans*-**6** isomer.

Bicyclic homoallylic alcohols **6** and **7** obtained by the above procedure were subsequently transformed in three steps to annelated furanosesquiterpenoids (*cf.* Refs. 11 and 19). These stages included epoxidation of the olefins to the respective epoxyalcohols and oxidation of the latter to epoxyaldehydes, followed by their transformation to the target furans (Scheme 2).

The first stage using *m*-chloroperbenzoic acid (MCPBA) resulted in stereospecific formation of compounds **8** and **9** from hydroxyolefins **6**. The original octalin **7** afforded a mixture of stereoisomers **13** (1α/1β ≈ 3), crystallization of which gave the pure α-isomer. Oxidation of epoxyalcohols **8**, **9**, and 1α-**13** with a pyridine—CrO_3 complex at the next stage gives unstable aldehydes. Without additional purification, the latter are transformed in 60—80 % overall yields by short contact with a tenfold (by weight) amount of SiO_2 in the absence of a solvent to give a mixture of furans (**10**,**14**) and unsaturated aldehydes (**11**,**12**,**15**) in ~1:1 ratio. The resulting mixture is easily separable by chromatography.

The structures of regular sesquiterpenoids **8**—**15** were established by spectral data. Among these compounds, only (±)-4*a*-epipallescensin A (**14**) has been partially reported in the form of both enantiomers[9] whose ^{1}H NMR spectra practically coincide with that of the racemate. The observed nonequivalence of protons of the *gem*-dimethyl group, which is typical of *cis*-coupled structures, is also observed in the ^{1}H NMR spectrum of furan *cis*-**10** containing separate signals for CH_3-C(8) in the δ ≈ 0.7—1.0 region. On the other hand, according to the literature data for pallescensin A (**1**),[4–10] the signals of the same protons in the spectrum of its regioisomer *trans*-**10** almost coincide. It should be noted that the above conclusion on the structure of octalins **6**,**7** and hence regioisomeric furans **10**,**14** agrees well with the

Scheme 2



Reagents and conditions: *a*, MCPBA/CH_2Cl_2, 0 °C; *b*, $CrO_3 \cdot 2Py/CH_2Cl_2$, 25 °C; *c*, SiO_2, 25 °C.

data of their mass spectra which display intense peaks with *m/z* 94 that result from the retrodiene decay of the molecular ion (*cf.* Ref. 2a).

The deduction on the stereochemistry of the *A/B*-coupling for tricyclic furans **10** and **14**, and hence the original epoxides **8, 9**, and **13**, was based on the above conclusion on the structures of their common precursors **6** and **7**. The relative configurations of the C(3) and C(1) centers in the molecules of epoxyalcohols **8, 9**, and **13** and the respective allyl alcohols **11, 12**, and **15** were revealed by the NOE, coupling constants, and conformational analysis of molecular models for these compounds by molecular mechanics[20] (Table 1). For example, observation of a significant NOE for $H_3C(11)$ and HC(3) of *cis*-epoxide **9** existing in a non-steroid conformation (*cf.* Ref. 21) is a reliable indication that the O—C(3) bonds in the latter and hence in alcohol **12** are β-oriented. The conclusion that the O—C(3) bond in compound *trans*-**8** is α-oriented was made on the basis of two vicinal coupling constants, $^3J_{3,4} \approx J_{3,4'} \approx$ 3 Hz, in the ^1H NMR spectrum of the respective alcohol **11** (the calculated values are $^3J_{3,4} = 3.26$ Hz, $J_{3,4'} \approx 3.14$ Hz) indicating that the proton at C(3) is in the equatorial position. According to the data in Tables 1—3 and in Fig. 1, compound **13** in solution is predominantly in the steroid conformation. Therefore, the presence of the remote *W*-constant $^4J = 0.9$ Hz indicates that the C(1) center in compound 1β-**13** has a β-configuration and hence this center in compound 1α-**13**, and in hydroxyaldehyde **15** obtained from it, has an α-configuration. Moreover, the observation of the NOE between the HC(1) and $H_3C(13)$ protons is additional evidence that the C(1)—O bond in hydroxyaldehyde **15** has an α-orientation.

Table 1. Results of the conformational analysis of compounds **6, 7, 9, 12, 13,** and **15** by molecular mechanics[20] and vicinal coupling constants for some protons of these compounds[a]

Compound	Conformation[b]	*E* kcal mol^{-1}	$^3J_{calc}(4,4a)$ *cis*	$^3J_{calc}(4,4a)$ *trans*	$^3J_{exp}(4,4a)$ *cis*	$^3J_{exp}(4,4a)$ *trans*
trans-**6**[c]	—	22.32	4.38	12.16	5.1	12.0
cis-**6**	S	25.93	6.17	11.24	7.05	<1
	N	22.86	6.81	1.08		
7[d]	S	24.80	2.78	12.34	4.5	9.2
	N	23.63	5.66	1.80		
3β,4aβ-**9**	S	34.69	5.32	11.62	7.1	1.9
	N	32.86	6.23	1.48		
1β,4aβ-**13**	S	35.30	2.50	12.29	3.0	12.6
	N	36.12	4.45	2.48		
1α,4aβ-**13**	S	36.18	2.75	12.33	3.0	12.2
	N	37.11	5.27	1.88		
15	S	31.10	4.20	12.19	6.0	<1
	N	31.48	6.45	1.27		
trans-**10**[e]	—	28.89	4.52	12.16	5.4	12.7
cis-**10**[e]	S	32.72	6.46	11.16	7.0	1.41
	N	29.60	6.79	1.04		
14	S	31.28	2.71	12.32	4.4	6.5
	N	30.41	5.51	1.88		

[a] Conformation energies were calculated by the PCMODEL program. The calculated and experimental vicinal coupling constants (Hz) are given for $CDCl_3$ solutions unless specified otherwise.
[b] S, steroid; N, nonsteroid conformation.
[c] C_6D_6. [d] CD_3CN.
[e] The vicinal coupling constants are given for the protons at C(1) and C(8*a*).

Table 2. ^{13}C NMR chemical shifts calculated by the additive scheme[22] for different types of coupling of cycles *A* and *B*

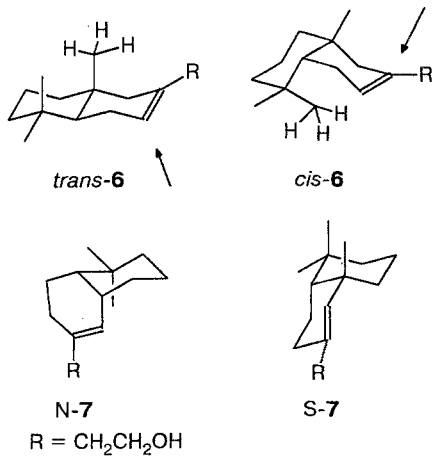
Type of *A/B* coupling	Conformation*	Atom C(8)	Atom C(7)	Atom C(6)
trans	—	40.24	18.48	42.26
cis	S	33.82	18.64	36.04
cis	N	40.24	18.72	40.24

* S, steroid; N, nonsteroid conformation.

Table 3. ^{13}C NMR spectra ($CDCl_3$) of compounds **6—15**

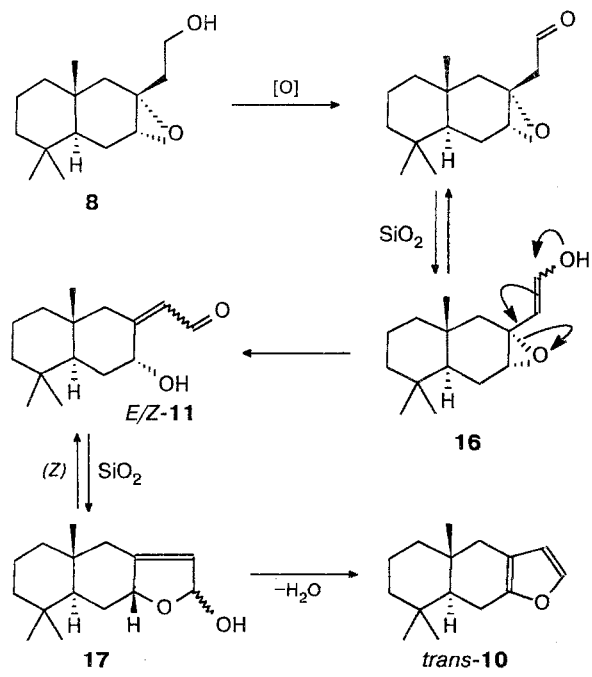
Atom C	*trans*-**6**	*cis*-**6**	**7**	**8**	**9**	*trans*-**10**	*cis*-**10**	**11**	**12**	α-**13**	β-**13**	**14**	**15**
1	48.64	36.61	35.55	48.56	35.79	21.62	20.76	42.70	36.96	70.47	68.53	157.20	73.50
2	132.01	32.10	34.01	61.00	61.30	150.31	149.57	163.63	167.65	61.94	61.71	114.96	168.10
3	123.32	22.77	28.20	58.70	56.56	114.94	115.30	73.81	70.25	28.67	30.90	21.48	26.12
4	23.76	23.73	20.93	22.88	22.17	42.02	31.29	31.18	33.98	20.59	18.98	20.81	23.63
4*a*	48.34	47.03	49.23	42.92	47.21	34.48	34.24	45.84	48.15	45.52	49.67	50.90	49.52
5	32.66	32.36	34.65	32.20	33.62	41.92	40.80	32.70	34.30	33.18	33.00	34.24	29.78
6	42.76	42.76	41.14	42.42	41.70	18.92	19.04	42.23	41.69	35.59	35.57	40.23	42.85
7	18.81	18.72	20.34	18.58	18.61	42.64	42.86	19.08	18.70	18.28	17.70	19.47	18.41
8	41.45	40.64	40.30	41.77	41.88	33.44	33.95	41.71	40.23	30.75	29.80	35.35	41.72
8*a*	32.75	33.85	35.93	32.49	31.69	49.64	49.82	37.85	37.59	34.10	33.73	35.97	35.18
9	40.76	41.07	41.69	40.03	37.86	140.44	140.34	127.21	123.69	39.11	37.40	139.85	123.58
10	60.13	60.22	61.27	59.02	58.82	110.67	110.59	191.42	190.77	59.08	59.20	110.01	190.48
11	32.80	21.27	27.10	32.61	23.01	33.19	20.85	32.80	26.90	26.95	32.00	26.96	24.34
12	19.14	33.28	32.74	20.14	33.00	21.92	33.43	18.85	33.24	30.80	31.30	32.29	33.40
13	21.33	31.74	32.65	22.00	32.26	19.27	31.48	21.16	31.20	32.16	29.34	30.19	27.64

The observed stereochemical result of the epoxidation of octalins **6** and **7** follows from the peculiarities of their structure (*cf.* Ref. 23). For example, when the molecular models of these compounds are considered, it becomes evident that β-attack by a the reagent on the compound *trans-A/B* **6** is spatially hindered due to shielding of this side of the molecule by the $H_3C(13)$ group, whereas the α-attack of compound *cis*-**6**, which is in a non-steroid conformation, is hindered by the proximity of the $H_3C(11)$ group to the C=C double bond. Furthermore, low-temperature (219 K) ^{13}C NMR experiments confirmed that this conformation of *cis*-**6** is predominant (>99 %). As was mentioned above, the reaction starting from octalin **7** results in a mixture of stereoisomers **13**, which is attributable to the existence of two conformers in the ratio N-**7**/S-**7** ≈ 7:3 in the reaction mixture. This ratio was estimated by calculating the *trans*-$^3J_{4',4a}$ constant according to the formula $p^N = (J^E - J^S)/(J^N - J^S)$, where p^N is the fraction of the non-steroid conformer in the mixture; J^E, J^N, and J^S are the values of the experimentally observed constant (averaged over the two conformations) and the constants for the non-steroid and steroid conformations, respectively.



The fact that approximately equal amounts of furans **10** and **14** and aldehydoalcohols **11**, **12**, and **15** incapable of furanization in the *E*-form are formed indicate the absence of stereoselectivity at the stage of SiO_2-initiated isomerization of intermediate epoxyaldehydes, *e.g.*, enol **16** corresponding to alcohol **8**. Moreover, this implies the sufficiently rapid dehydration of the **17**-type cyclic form of the *Z*-isomers of the above aldehydes (Scheme 3). The open form of one of them, *Z*-**11**, could be detected in the aldehyde fraction enriched with this unstable compound. This fraction was isolated by flash-chromatography of the reaction mixture produced

Scheme 3



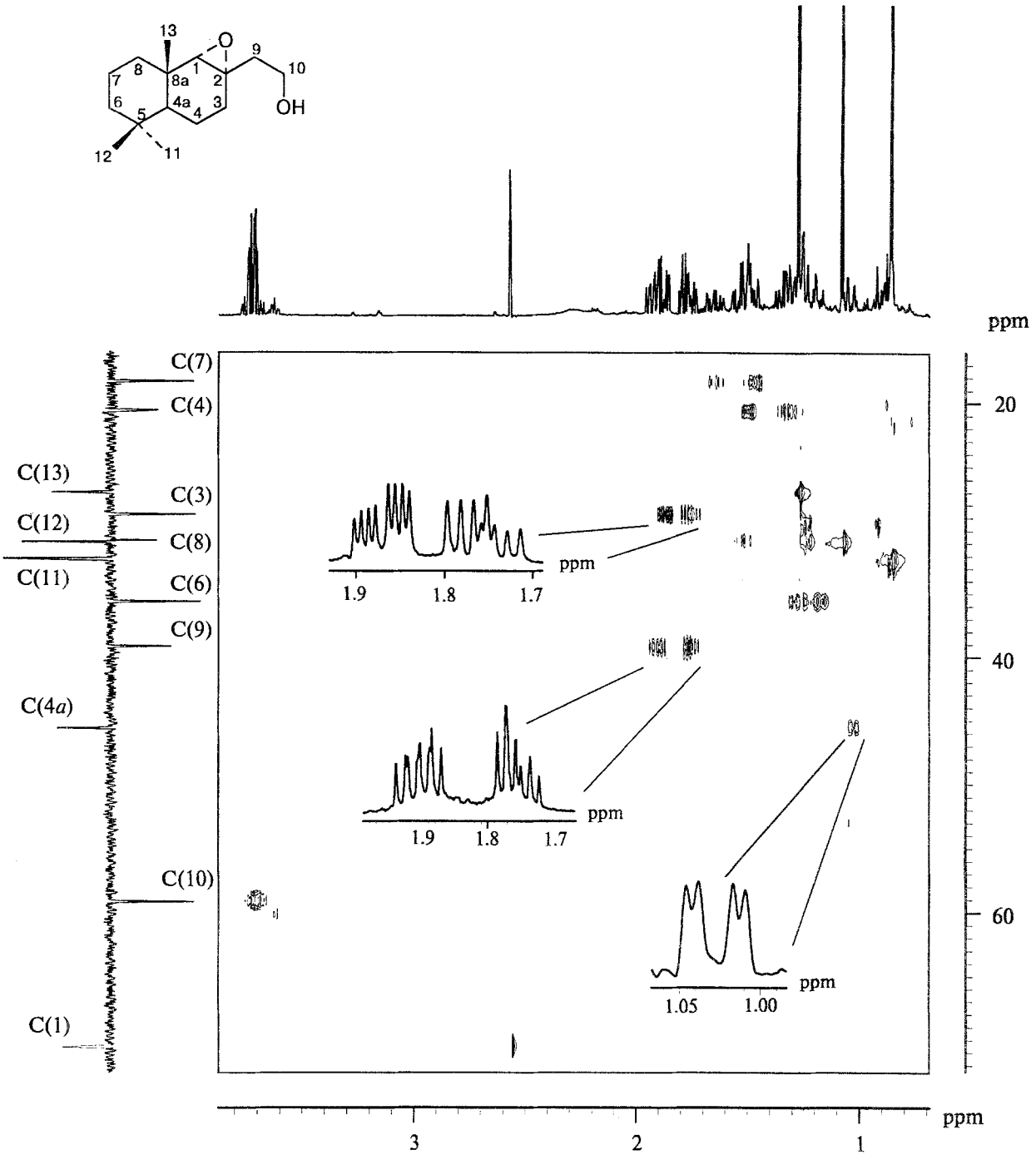


Fig. 1. *z*-HMQC $^1H—^{13}C$ NMR spectrum of compound 1α-**13** (Bruker AMX-400, $CDCl_3$, ~25 °C). ^1H and ^{13}C NMR spectra (DEPT-135) are given along the axes. This spectrum is an example of the use of multiquantum spectroscopy for obtaining homonuclear coupling constants. Such experiments were performed with compounds **6**, **7**, **9**, **12**, **13**, and **15**.

from compound **8**. In agreement with the structure of *Z*-**11**, the signal for HC(3) in its ^1H NMR spectrum (br.t, δ 5.42, J = 3 Hz) is shifted downfield by $\Delta\delta \approx 1.1$ in comparison with the similar signal for stereoisomer *E*-**11**, while the parameters of the resonance signals of olefin (br.d, δ 5.78, J = 8.3 Hz) and formyl (d, δ 10.03, J = 8.3 Hz) protons are close. It should be noted that stereoisomer *E*-**11** is slowly transformed on storage to give furan *trans*-**10**.

Thus, a simple scheme for transforming farnesanes having a methylene group in the α-isoprenoid unit to tricyclic furanosesquiterpenoids has been proposed.

Experimental

Melting points were determined on a Kofler hot stage and were not corrected. IR spectra (ν/cm^{-1}) were obtained on Specord M-80 and Perkin-Elmer 577 spectrophotometers in thin layers.* ^1H and ^{13}C NMR spectra (δ) for $CDCl_3$ solutions were recorded on Bruker WM-250, Bruker AM-300, and Bruker AMX-400 spectrometers. DQF-COSY,[24] NOESY,[25] HMQC,[26] and *z*-HMQC[27] (H-detected multiple-quantum coherence with z-filter) spectra were recorded on a Bruker AMX-400 spectrometer. Mass spectra {EI, 70 eV, m/z (I_{rel}, %)} were obtained on a Varian MAT CH-6 instrument. The R_f values refer to a fixed SiO_2 layer (Silufol). HPLC was performed on a Silasorb 600 column (10 mm, 250×24 mm).

3-Methylene-7*Z*,11-dimethyl-6,10-dodecadien-1-ol (*Z*-4), 3-methylene-7*E*,11-dimethyl-6,10-dodecadien-1-ol (*E*-4), and 3-methyleno-5-(1′,6′6′-trimethyl-2′-cyclohexenyl)-1-pentanol (5). A mixture of a 1.3 *M* solution of *n*-BuLi in hexane (30 mL, 39 mmol) and TMEDA (5.88 mL, 39 mmol) was stirred at 25 °C (Ar) for 30 min and then treated at −10 °C for 10 min with a solution of isobutenylcarbinol **3** (1.68 g, 19.5 mmol) in hexane (7 mL). The reaction mixture was stirred for 12 h at 25 °C and then treated for 5 min at −70 °C with a solution of neryl chloride[28] (2.59 g, 15 mmol) in THF (15 mL). After 1 h, the reaction mixture was heated to 25 °C over 20 min, decomposed with aqueous saturated NH_4Cl (20 mL), and extracted with ether. The extract was washed with water, dried with Na_2SO_4, and concentrated *in vacuo*. The residue (3.5 g) was chromatographed on SiO_2 (100 g). Elution with a hexane—ether mixture (7:3) gave 2.03 g (61 %) of compound *Z*-**4**,[12] b.p. 90—93 °C (0.07 Torr), n_D^{20} 1.4832. ^1H NMR: 1.62 and 1.69 (br.s, 9 H, CH_3); 1.9—2.2 (m, 8 H, CH_2); 2.30 (br.t, J = 6.5 Hz, 2 H, CH_2); 3.71 (br.t, J = 6.5 Hz, 2 H, CH_2O); 4.84 and 4.87 (br.s, 2 H, H_2C=C); 5.12 (m, 2 H, HC=C). Found (%): C, 81.07; H, 11.79. $C_{15}H_{26}O$. Calculated (%): C, 81.02; H, 11.79.

A similar reaction starting from carbinol **3** (1.46 g) and geranyl chloride[28] (1.46 g) gave 1.34 g (71 %) of product *E*-**4**,[11] b.p. 87—89 °C (0.05 Torr), n_D^{20} 1.4855. ^1H NMR: 1.63 and 1.69 (br.s, 9 H, CH_3); 1.9—2.2 (m, 8 H, CH_2), 2.32 (br.t, J = 6.5 Hz, 2 H, CH_2); 3.72 (br.t, J = 6.5 Hz, 2 H, CH_2O); 4.84 and 4.87 (br.s, 2 H, H_2C=C); 5.12 (m, 2 H, HC=C).

A similar reaction starting from carbinol **3** (1.38 g) and α-cyclogeranyl bromide[29] (1.58 g) resulted in 1.22 g (75 %) of compound **5**, b.p. 91—94 °C (0.08 Torr), n_D^{20} 1.4914. IR: 820, 865, 900, 940, 995, 1050, 1130, 1180, 1235, 1340, 1365, 1380, 1450, 1640, 2870—2980, 3080, 3620. ^1H NMR: 0.88 and 0.93 (s, 6 H, CH_3); 1.68 (br.s, 3 H, CH_3); 1.1—1.7 (m, 4 H, CH_2), 1.9—2.1 (m, 5 H, CH, CH_2), 2.31 (br.t, J = 6.5 Hz, 2 H, CH_2); 3.71 (br.t, J = 6.5 Hz, 2 H, CH_2O); 4.81 and 4.87 (br.s, 2 H, H_2C=C); 5.30 (m, 2 H, HC=C). Found (%): C, 81.27; H, 11.79. $C_{15}H_{26}O$. Calculated (%): C, 81.02; H, 11.79.

2-(2′-Hydroxyethyl)-5,5,8*a*β-trimethyl-1,4,4*a*α,5,6,7,8,8*a*-octahydronaphthalene (*trans*-6), 2-(2′-hydroxyethyl)-5,5,8*a*β-trimethyl-1,4,4*a*β,5,6,7,8,8*a*-octahydronaphthalene (*cis*-6), and 2-(2′-hydroxyethyl)-5,5,8*a*β-trimethyl-3,4,4*a*β,5,6,7,8,8*a*-octahydronaphthalene (7). $F_3B \cdot OEt_2$ (1.87 mL, 15.2 mmol) was added over 15 min at 0 °C (Ar) to a vigorously stirred solution of alcohol *Z*-**4** (1.15 g, 5.2 mmol) in hexane (20 mL). The reaction mixture was heated to 25 °C over 10 min. After 20 min the mixture was decomposed with saturated aqueous $NaHCO_3$ and extracted with hexane. The extract was washed with water, dried with Na_2SO_4, and concentrated *in vacuo*. The residue (1.18 g) was chromatographed on 30 g of SiO_2. Elution with a hexane—ether mixture (4:1) gave 0.99 g (86 %) of alcohols **6** and **7** as a light-yellow oil, R_f 0.37 (hexane—ether, 4:1) further separated by semipreparative HPLC (13 % AcOEt in heptane as the eluent). The elution successively gave compounds *cis*-**6** (0.5 g, 44 %), **7** (0.14 g, 12 %), and *trans*-**6** (80 mg, 7 %).

Octalin *trans*-**6** is a colorless oil, b.p. 94—95 °C (0.1 Torr), n_D^{20} 1.5092. IR: 810, 830, 860, 890, 935, 980, 1005, 1045, 1120, 1170, 1230, 1270, 1345, 1370, 1380, 1390, 1430—1470, 2840—3000, 3340. ^1H NMR (C_6D_6): 0.93 (s, 3 H, H_3C-11); 0.94 (d, J = 0.5 Hz, 3 H, H_3C-12); 0.96 (t, J = 0.8 Hz, 3 H, H_3C-13); 1.13 (td, J = 12.8 Hz and 3.7 Hz, 1 H, H_aC-8); 1.24 (m, 1 H, H_aC-6); 1.25 (dd, J = 12.0 Hz and 5.1 Hz, 1 H, HC-4*a*); 1.47 (m, 1 H, H_eC-6); 1.49 (m, 1 H, H_eC-7); 1.58 (m, 1 H, H_eC-8); 1.72 (AB, J_{AB} = 15.5 Hz, 2 H, H_2C-1, Δδ 0.17); 1.75 (m, 1 H, H_aC-7); 1.92 (m, 1 H, H_2C-4); 2.23 (t, J = 6.6 Hz, 2 H, H_2C-9); 3.68 (t, J = 6.6 Hz, 2 H, CH_2O); 5.52 (m, 1 H, HC=C). Found (%): C, 81.18; H, 11.85. $C_{15}H_{26}O$. Calculated (%): C, 81.02; H, 11.79.

Octalin *cis*-**6** is a colorless oil, b.p. 96—97 °C (0.1 Torr), n_D^{20} 1.5068. IR: 820, 880, 980, 1045, 1190, 1340, 1370, 1390, 1430—1470, 2840—2980, 3340. ^1H NMR: 0.76 (s, 3 H, H_3C-11); 0.86 (s, 3 H, H_3C-13); 0.89 (s, 3 H, H_3C-12); 1.07 (br.d, J = 7.05 Hz, 1 H, HC-4*a*); 1.15 (m, 1 H, H_aC-6); 1.18 (m, 1 H, H_aC-8); 1.34 (m, 1 H, H_eC-7); 1.36 (m, 1 H, H_eC-6); 1.40 (m, 1 H, H_eC-8); 1.49 (m, 1 H, H_aC-7); 1.77 (AB, J_{AB} = 13.5 Hz, Δδ 0.5, 2 H, H_2C-1); 2.08 (m, 1 H, H_aC-4); 2.22 (m, 1 H, H_eC-4); 2.17 (t, J = 6.4 Hz, 2 H, H_2C-9); 3.61 (t, J = 6.4 Hz, 2 H, CH_2O); 5.43 (m, 1 H, HC=C). Found (%): C, 81.22; H, 11.82. $C_{15}H_{26}O$. Calculated (%): C, 81.02; H, 11.79.

Octalin **7** is a colorless oil, b.p. 95 °C (bath) (0.02 Torr), n_D^{20} 1.5075. IR: 845, 875, 920, 950, 980, 1045, 1340, 1365, 1370, 1390, 1420—1470, 2840—3000, 3340. ^1H NMR (CD_3CN): 0.87 (m, 1 H, H_aC-6); 0.92 (s, 3 H, H_3C-11); 1.01 (s, 3 H, H_3C-12); 1.04 (s, 3 H, H_3C-13); 1.17 (dd, J = 9.2 Hz and 4.5 Hz, 1 H, HC-4*a*); 1.26 (m, 1 H, H_eC-6); 1.27 (m, 1 H, H_aC-8); 1.42 (m, 2 H, H_2C-7); 1.47 (m, 1 H, H_eC-8); 1.74 (m, 1 H, H_aC-4); 1.91 (m, 1 H, H_eC-4); 1.96 (m, 2 H, H_2C-3); 2.09 (td, J = 7.2 Hz and 0.7 Hz, 2 H, H_2C-9); 3.62 (t, J = 7.2 Hz, 2 H, CH_2O); 5.18 (m, 1 H, HC=C). MS: 222 $[M]^+$ (35), 208 (20), 207 (100), 189 (16), 179 (12), 178 (20), 177 (35), 151 (10), 137 (35), 135 (21), 125 (27), 121 (25), 119 (27), 109 (27), 105 (25), 95 (27), 93 (27), 91 (27), 81 (35), 79 (25), 69 (27), 67 (16), 55 (27), 41 (27). Mol. weight calculated for $C_{15}H_{26}O$: 222.4.

In a similar manner, the procedure starting from carbinol *E*-**4** (1.34 g, 6.0 mmol) and $F_3B \cdot OEt_2$ (2.55 g, 18.0 mmol) in hexane (22 mL) gave 1.14 g (85 %) of alcohols **6** which were separated by semipreparative HPLC (13 % AcOEt in heptane as the eluent). Elution successively gave 0.14 g (10.5 %) of compound *cis*-**6** and 0.71 g (53 %) of *trans*-**6** identical to the samples of these compounds described above.

$F_3B \cdot OEt_2$ (1.76 g, 13.6 mmol) was added over 10 min at 0 °C to a stirred solution of alcohol **5** (1.32 g, 5.9 mmol) in CH_2Cl_2 (13 mL). The reaction mixture was heated to 25 °C over 10 min. 30 min later the mixture was decomposed with saturated aqueous $NaHCO_3$ and extracted with ether. Subsequent ordinary treatment of the extract gave 1.4 of a product which was then chromatographed on SiO_2 (50 g). Elution with a hexane—ether mixture (4:1) gave 0.82 g (62 %) of alcohols

* Unless specified otherwise.

6 and **7** which was separated by semipreparative HPLC (13 % AcOEt in heptane as the eluent). Elution successively gave compounds *cis*-**6** (0.3 g, 22 %), **7** (90 mg, 7 %), and *trans*-**6** (90 mg, 7 %) identical to the samples of these compounds described above.

2α,3α-Epoxy-2β-(2′-hydroxyethyl)-5,5,8*a*β-trimethyl-1,2,3,4,4*a*α,5,6,7,8,8*a*-decahydronaphthalene (8). MCPBA (0.59 g, 3.4 mmol) was added over 10 min at 0 °C (Ar) to a stirred solution of alcohol *trans*-**6** (0.63 g, 2.83 mmol) in CH_2Cl_2 (13 mL). After 1 h, the reaction mixture was diluted with ether, washed with 5 % KOH and water, dried with Na_2SO_4, and concentrated *in vacuo*. The residue (0.67 g) was chromatographed on SiO_2 (20 g). Elution with a hexane—ether mixture (7:3) gave 0.59 g (87 %) of epoxide **8** as colorless prisms, m.p. 49—50 °C (hexane). IR ($CHCl_3$): 840, 860, 920, 940, 965, 980, 995, 1040, 1055, 1090, 1120, 1140, 1165, 1220, 1275, 1315, 1345, 1370, 1385, 1390, 1445, 1460, 1660, 2850—3000, 3460, 3610. ^{1}H NMR: 0.82 and 0.85 (s, 9 H, CH_3); 0.9—2.1 (m, 13 H, CH, CH_2); 3.22 (t, J = 2.1 Hz, 1 H, HC-3); 3.65 (t, J = 6.1 Hz, 2 H, CH_2O). MS: 238 $[M]^+$. Found (%): C, 75.63; H, 10.84. $C_{15}H_{26}O_2$. Calculated (%): C, 75.58; H, 10.99, mol. weight 238.4.

2β,3β-Epoxy-2α-(2′-hydroxyethyl)-5,5,8*a*β-trimethyl-1,2,3,4,4*a*β,5,6,7,8,8*a*-decahydronaphthalene (9). A similar procedure starting from *cis*-**6** (0.88 g) gave 0.75 g (80 %) of epoxide **9** as colorless prisms, m.p. 43—44 °C (hexane). IR ($CHCl_3$): 840, 860, 880, 900, 910, 935, 945, 960, 980, 1025, 1045, 1070, 1110, 1145, 1165, 1220, 1360, 1375, 1390, 1430, 1470, 1660, 2850—2990, 3480, 3610. ^{1}H NMR : 0.79, 0.88 and 0.98 (s, 9 H, CH_3); 1.00 (dd, J = 7.1 Hz and 1.9 Hz, 1 H, HC-4*a*); 1.1—2.2 (m, 12 H, CH_2); 3.17 (br.d, J = 6.1 Hz, 1 H, HC-3); 3.67 (m, 2 H, CH_2O). MS: 238 $[M]^+$ Found (%): C, 75.77; H, 11.10. $C_{15}H_{26}O_2$. Calculated (%): C, 75.58; H, 10.99, mol. weight 238.4.

1α,2α-Epoxy-2α-(2′-hydroxyethyl)-5,5,8*a*β-trimethyl-1,2,3,4,4*a*β,5,6,7,8,8*a*-decahydronaphthalene (1α-13) and 1β,2β-epoxy-2α-(2′-hydroxyethyl)-5,5,8*a*β-trimethyl-1,2,3,4,4*a*β,5,6,7,8,8*a*-decahydronaphthalene (1β-13). The procedure as described for compound **8** starting from olefin **7** (0.2 g) gave 0.18 g (84 %) of epoxides **13** separated by semipreparative HPLC (35 % AcOEt in heptane as the eluent). The elution successively gave compounds 1β-**13** (43 mg, 20 %) and 1α-**13** (128 mg, 60 %).

Epoxide 1α-**13**: colorless prisms, m.p. 42—43 °C (hexane). IR ($CHCl_3$): 850, 880, 890, 920, 970, 990, 1030, 1060, 1100, 1225, 1320, 1345, 1360, 1380, 1390, 1430, 1490, 2820—3010, 3430. ^{1}H NMR: 0.86 (s, 3 H, H_3C-11); 1.03 (dd, J = 12.2 Hz and 3.0 Hz, 1 H, HC-4*a*); 1.08 (s, 3 H, H_3C-12); 1.17—1.30 (m, 2 H, H_2C-6); 1.27 (s, 3 H, H_3C-13); 1.28 (m, 1 H, HC-8); 1.32 (m, 1 H, H_aC-4); 1.47 (m, 1 H, HC-7); 1.51 (m, 1 H, H_eC-4); 1.53 (m, 1 H, HC-8); 1.66 (m, 1 H, HC-7); 1.76 (m, 1 H, HC-9); 1.77 and 1.86 (m, 2 H, H_2C-3); 1.92 (m, 1 H, HC-9); 2.57 (br.s, 1 H, HCO); 3.72 (m, 2 H, CH_2O). MS: 238 $[M]^+$ (1), 220 (4), 208 (34), 193 (21), 177 (12), 175 (13), 138 (22), 137 (59), 136 (16), 125 (16), 124 (21), 123 (69), 121 (22), 109 (31), 95 (44), 85 (65), 84 (63), 83 (100), 81 (44), 71 (22), 69 (53), 67 (23), 55 (34), 47 (25), 43 (15), 41 (34). Mol. weight calculated for $C_{15}H_{26}O_2$: 238.4.

Epoxide 1β-**13** is a colorless oil, R_f 0.45 (hexane—ether, 1:4). ^{1}H NMR: 0.82 (dd, J = 12.6 Hz and 3.0 Hz, 1 H, HC-4*a*); 0.86 (s, 3 H, H_3C-11); 1.08 (s, 3 H, H_3C-12); 1.17 (s, 3 H, H_3C-13); 1.21 (m, 2 H, H_2C-6); 1.25 (m, 1 H, H_aC-8); 1.3—1.4 (m, 2 H, H_2C-4); 1.58 (ddd, J = −14.4 Hz, 12.2 Hz, and 4.5 Hz, 1 H, H_aC-3); 1.72 (dt, J = 13.2 Hz and 4.7 Hz, 1 H, H_eC-8); 1.89 and 1.94 (ddd, J_H = −14.7 Hz, 7.3 Hz, and 5.5 Hz; $J_{H'}$ = −14.7 Hz, 6.0 Hz, and 4.8 Hz, 2 H, H_2C-9); 2.04 (ddt, J = −14.4 Hz, 3.4 Hz, and 0.9 Hz, 1 H, H_eC-3); 2.66 (d, ^4J = 0.9 Hz, 1 H, HC-1); 3.74 (m, 2 H, CH_2O).

4*a*β,8,8-Trimethyl-1,4,4*a*,5,6,7,8,8*a*α-octahydronaphtho-[2,3-*b*]furan (*trans*-10) and 2-(2′*E*-formylmethyleno)-3α-hydroxy-5,5,8*a*β-trimethyl-1,2,3,4,4*a*α,5,6,7,8,8*a*-decahydronaphthalene (11). A solution of epoxide **8** (0.48 g, 2 mmol) in CH_2Cl_2 (5 mL) was added with stirring (25 °C, Ar) over 3 min to a complex freshly prepared[30] from CrO_3 (1.2 g, 12 mmol) and pyridine (1.9 g, 24 mmol) in CH_2Cl_2 (15 mL). After 1 h the reaction mixture was diluted with ether, the solution was separated, and the precipitate was washed with ether. The combined solution was filtered through a thin SiO_2 layer (~1 g) and concentrated *in vacuo*. The residue (0.44 g) was mixed with SiO_2 (4.5 g), kept for 4 h at 25 °C, and extracted with ether. The product (0.41 g) obtained after removing the solvent was chromatographed on SiO_2 (30 g). Elution with hexane and a hexane—ether mixture (3:2) successively gave compounds *trans*-**10** (0.17 g, 38 %) and **11** (0.13 g, 27 %).

Furan *trans*-**10** is a colorless liquid, m.p. 105 °C (in a bath; 0.02 Torr), n_D^{20} 1.5137. IR: 600, 640, 695, 725, 785, 840, 900, 980,1035, 1095, 1110, 1130, 1145, 1175, 1200, 1230, 1270, 1295, 1305, 1325, 1345, 1365, 1380, 1390, 1420, 1440, 1470, 1505, 1555, 1640, 2850—3000. ^{1}H NMR: 0.92 (s, 3 H, H_3C-13); 0.98 (s, 3 H, H_3C-11); 1.00 (s, 3 H, H_3C-12); 1.28 (m, 1 H, HC-7); 1.30 (m, 1 H, HC-5);1.47 (m, 1 H, HC-6); 1.48 (dd, J = 12.7 Hz and 5.4 Hz, 1 H, HC-8*a*); 1.53 (m, 1 H, HC-7); 1.67 (m, 1 H, HC-6); 1.68 (m, 1 H, HC-5); 2.19 (AB, J_{AB} = 15.4 Hz, 2 H, H_2C-4, Δδ 0.06); 2.42 and 2.72 (m, 2 H, HC-1); 6.17 (br.d, J = 1.9 Hz, 1 H, HC-10); 7.26 (br.d, J = 1.9 Hz, 1 H, HC-9). MS: 218 $[M]^+$ (32), 203 (10), 149 (17), 137 (8), 135 (13), 134 (10), 133 (8), 131 (8), 125 (8), 124 (8), 123 (17), 121 (8), 111 (12), 109 (22), 107 (8), 105 (10), 97 (22), 95 (23), 94 (100), 85 (17), 83 (20), 81 (20), 71 (30), 69 (32), 57 (35), 55 (22), 43 (30), 41 (20), 40 (20). Mol. weight calculated for $C_{15}H_{22}O$: 218.3.

Aldehyde **11** was obtained as colorless prisms, m.p. 119—120 °C (hexane). IR (KBr): 570, 650, 665, 690, 720, 775, 820, 855, 875, 930, 945, 955, 975, 1015, 1040, 1055, 1075, 1090, 1120, 1145, 1165, 1205, 1240, 1285, 1310, 1350, 1370, 1385, 1405, 1440, 1460, 1680, 2840—3000, 3470. ^{1}H NMR: 0.81, 0.85 and 0.91 (s, 9 H, CH_3); 1.2—2.0 (m, 9 H, CH, CH_2); 2.52 (AB, J_{AB} = 13.0 Hz, Δδ 0.17, 2 H, H_2C-1); 4.35 (br.t, J = 3.0 Hz, 1 H, HC-3); 5.96 (dd, J = 8.2 Hz and 1.5 Hz, 1 H, HC=C); 9.98 (d, J = 8.2 Hz, 1 H, CHO). MS: 236 $[M]^+$. Found (%): C, 76.00; H, 10.11. $C_{15}H_{24}O_2$. Calculated (%): C, 76.22; H, 10.24, mol. weight 236.4.

4*a*β,8,8-Trimethyl-1,4,4*a*,5,6,7,8,8*a*β-octahydronaphtho-[2,3-*b*]furan (*cis*-10) and 2-(2′*E*-formylmethyleno)-3β-hydroxy-5,5,8*a*β-trimethyl-1,2,3,4,4*a*β,5,6,7,8,8*a*-decahydronaphthalene (12). A similar procedure starting from compound **9** (0.53 g, 2.2 mmol), CrO_3 (1.32 g, 13.2 mmol), and pyridine (2.08 g, 26.4 mmol) gave 0.50 g of a compound. The latter was kept with SiO_2 (5.0 g), and the product was chromatographed on SiO_2 (30 g) to afford 0.21 g (43 %) of *cis*-**10** and 0.19 g (36 %) of **12**.

Furan *cis*-**10** is a colorless liquid, b.p. (on a bath) 95 °C (0.02 Torr), n_D^{20} 1.5122. IR: 600, 630, 680, 725, 750, 820, 840, 900, 980, 1040, 1090, 1130, 1150, 1170, 1180, 1205, 1225, 1270, 1310, 1330, 1350, 1360, 1370, 1380, 1390, 1420, 1470, 1505, 1555, 1640, 2840—2990. ^{1}H NMR: 0.65 (s, 3 H, H_3C-11); 0.97 (s, 3 H, H_3C-12); 1.00 (s, 3 H, H_3C-13); 1.27 (m, 1 H, HC-7); 1.36 (m, 1 H, HC-5); 1.41 (br.d, J = 7.0 Hz, 1 H, HC-8*a*); 1.46 (m, 1 H, HC-7); 1.47 (m, 1 H, HC-6); 1.58 (m, 1 H, HC-5); 1.70 (m, 1 H, HC-6);

2.36 (AB, J_{AB} = 16.0 Hz, Δδ 0.41, 2 H, HC-4); 2.72 (m, 2 H, HC-1); 6.16 (br.d, J = 2.0 Hz, 1 H, HC-10); 7.26 (br.d, J = 2.0 Hz, 1 H, HC-9). MS: 218 $[M]^+$ (22), 149 (13), 135 (13), 134 (8), 133 (4), 109 (13), 107 (8), 105 (13), 94 (100), 85 (28), 83 (40), 69 (20), 57 (15), 55 (15), 43 (28), 41 (25). Mol. weight calculated for $C_{15}H_{22}O$: 218.3.

Aldehyde **12** was obtained as colorless needles, m.p. 113—114 °C (hexane). IR (KBr): 565, 580, 630, 660, 770, 820, 845, 860, 880, 915, 930, 940, 980, 1040, 1055, 1080, 1090, 1130, 1150, 1170, 1190, 1220, 1240, 1255, 1290, 1330, 1360, 1380, 1390, 1415, 1445, 1480, 1645, 1680, 2840—2995, 3380. ^{1}H NMR: 0.95, 1.00, and 1.06 (s, 9 H, CH_3); 1.1—2.2 (m, 9 H, CH, CH_2); 2.64 (AB, J_{AB} = 13.9 Hz, Δδ 0.08, 2 H, HC-1); 4.46 (dd, J = 10.9 Hz and 6.2 Hz, 1 H, HC-3); 6.29 (br.d, J = 8.3 Hz, 1 H, HC=C); 9.96 (d, J = 8.3 Hz, 1 H, CHO). MS: 236 $[M]^+$. Found (%): C, 76.10; H, 10.35. $C_{15}H_{24}O_2$. Calculated (%): C, 76.22; H, 10.24, mol. weight 236.4.

5,5,8*a*β-Trimethyl-3,4,4*a*β,5,6,7,8,8*a*-octahydronaphtho-[1,2-*b*]furan (*d,l*-4*a*-epipallescensin A, 14) and 2-(2′*E*-formylmethyleno)-1α-hydroxy-5,5,8*a*β-trimethyl-1,2,3,4,4*a*β,5,6,7,8,8*a*-decahydronaphthalene 15. The procedure described for compound **8** starting from compound 1α-**13** (0.12 g, 0.5 mmol), CrO_3 (0.30 g, 3 mmol), and pyridine (0.48 g, 6 mmol) followed by keeping the intermediate product (0.10 g) with SiO_2 (1 g) and chromatographic purification on SiO_2 (2 g) gave 32 mg (29 %) of compound **14** and 34 mg (29 %) of compound **15**.

Furan **14** is a colorless liquid, R_f 0.42 (hexane). IR ($CHCl_3$): 610, 705, 735, 840, 865, 880, 890, 900, 940, 960, 980, 1040, 1080, 1095, 1125, 1145, 1160, 1180, 1200, 1220, 1250, 1310, 1365, 1380, 1390, 1440, 1470, 1505, 1560, 1630, 2860—3020. ^{1}H NMR: 0.83 (s, 3 H, H_3C-11); 1.09 (s, 3 H, H_3C-12); 1.33 (s, 3 H, H_3C-13); 1.26 (m, 1 H, HC-6); 1.33 (m, 1 H, HC-6); 1.36 (m, 1 H, HC-7); 1.42 (dd, J = 6.5 Hz and 4.4 Hz, 1 H, HC-4*a*); 1.48 (m, 1 H, HC-8); 1.53 (m, 1 H, HC-7); 1.86 (dddd, J = −14.3 Hz, 7.2 Hz, 7.2 Hz, and 4.4 Hz, 1 H, HC-4); 2.07 (dddd, J = −14.3 Hz, 7.4 Hz, 6.5 Hz, and 5.6 Hz, 1 H, H′C-4); 2.10 (m, 1 H, HC-8); 2.42 (ddd, J = −16.3 Hz, 7.2 Hz, and 5.6 Hz, 1 H, H′C-3); 2.53 (ddd, J = −16.3 Hz, 7.4 Hz, and 7.2 Hz, 1 H, HC-3); 6.12 (d, J = 1.8 Hz, 1 H, HC-10); 7.23 (d, J = 1.8 Hz, 1 H, HC-9). MS: 218 $[M]^+$ (16), 204 (16), 203 (100), 182 (7), 175 (6), 147 (18), 135 (14), 134 (6), 133 (10), 121 (6), 119 (7), 105 (8), 91 (10), 81 (7), 77 (8), 69 (36), 57 (14), 55 (10),45 (18), 44 (36), 43 (15), 41 (20). Molecular weight calculated for $C_{15}H_{22}O$: 218.3.

Aldehyde **15** is a colorless oil, R_f 0.56 (ether—hexane, 4:1). IR ($CHCl_3$): 820, 865, 890, 950, 980, 1010, 1030, 1080, 1105, 1155, 1220, 1370, 1390, 1440, 1475, 1630, 1670, 2860—3020, 3450, 3610. ^{1}H NMR: 0.92, 1.02, and 1.07 (s, 9 H, CH_3); 1.2—3.2 (m, 11 H, CH, CH_2); 4.42 (br.s, 1 H, HC-1); 6.19 (br.d, J = 8.5 Hz, 1 H, HC=C); 10.06 (d, J = 8.5 Hz, 1 H, CHO). MS: 236 $[M]^+$ (3), 219 (11), 218 (18), 203 (100), 191 (5), 175 (7), 147 (23), 135 (18), 133 (11), 124 (14), 123 (15), 109 (35), 105 (11), 95 (14), 91 (15), 85 (20), 81 (18), 69 (58). Molecular weight calculated for $C_{15}H_{24}O_2$: 236.4.

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