Construction of Trinervitane and Kempane Skeletons Based on Biogenetical Routes[1)][2)]

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Based on the putative biogenesis of trinervitane- and kempane-type diterpenes (*Scheme 1*), a biogenetic-type transformation was simulated by cyclization of 7,16-secotrinervita-7,11,15-triene-2α,3α,17-triol (**23**) and of its 17-chloro derivative **30**. The requisite substrates were prepared from geranylgeranoic acid chloride **6** (*Schemes 2*, *4*, and *5*). Treatment of **30** with $AgClO_4$ at $-20°$ provided the trinervitantrienediols **32** and **33** in 68 and 5% yields, while kempadienediol **35** was obtained in 50% yield by the same reagent at $+20°$ (*Scheme 7*). The structures of the cyclization products were elaborated from detailed inspection of NMR spectra including H,H COSY, C,H COSY, and NOESY (*Tables 1* and *2*). The conformation of **30** and its plausible cyclization intermediate was discussed with the help of physical evidence, including X-ray crystallographic analysis.

Introduction. – Several species of termite soldiers inhabiting the tropics are known to secrete their defensive substances, from which a variety of cyclic diterpenes were characterized by the *Prestwich* and *Braekman* groups more than two decades ago [3]. The diterpenes are composed of bicyclic compounds [4], *e.g.*, 7,16-secotrinervita-triene-2,3-diol 2-acetate **3**, tricyclic compounds [5], *e.g.*, trinervitadiene-2,3-diol **4**, and tetracyclic compounds [6], *e.g.*, by 14-acetoxykempa-6,8-dien-3-one **5**. As shown in *Scheme 1*, a plausible biogenesis of these skeletons is suggested to start from geranylgeranyl-OPP **1** to give the 14-membered monocyclic neocembrene **2**, well known as a trail pheromone of the termite workers [7]. The six-membered-ring formation in **2** leads to the construction of a bicyclic secotrinervitatriene skeleton, which provides the common precursor for the further cyclization to the trinervitane and kempane skeletons. The intramolecular H-shift from C(1) to C(12) of the secotrinervitatriene skeleton, followed by migration of the C=C bond with concomitant formation of the five-membered ring (*Path a*) produces the trinervitadiene skeleton.

Path b shows a plausible route to the kempane skeleton, in which the initial protonation (or H-radical addition) at C(12) of the secotrinervitatriene skeleton accompanies the formation of an additional six-membered ring. The concomitant connection between C(7) and C(16) leads to the tetracyclic kempene framework[3)].

We have been much interested in the synthesis of biologically intriguing trinervitane and kempane skeletons based on the biogenetical route of *Scheme 1* and have achieved the synthesis of some secotrinervitane-type diterpenes starting from

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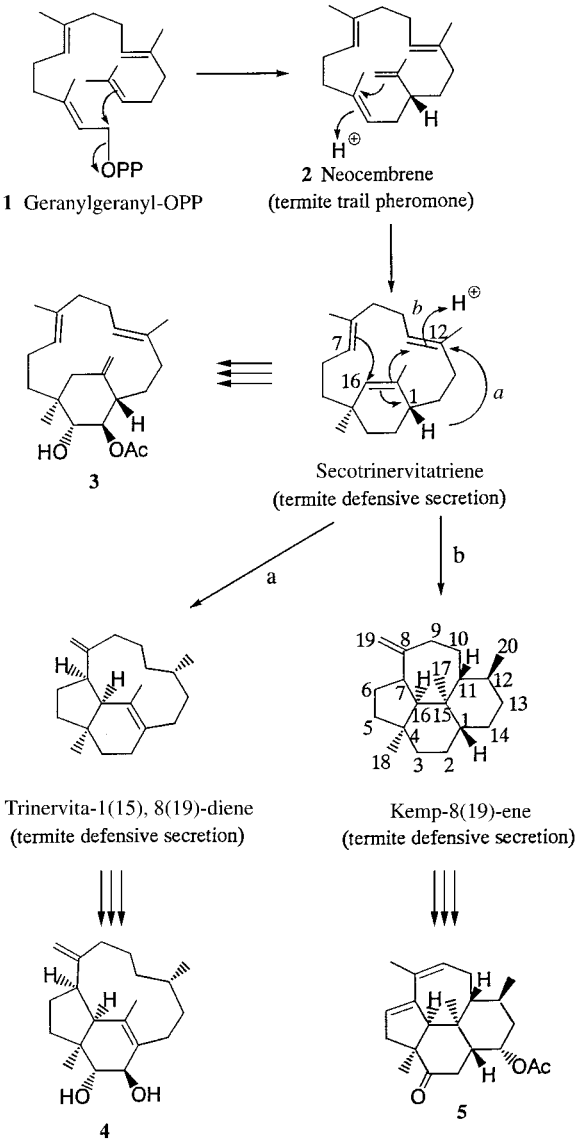
1) Part 60 of the series of cyclization of polyenes: for Part 59, see [1].
2) Partially published in a preliminary communication [2].
3) The numbering of the skeleton is based on those proposed by *Prestwich* and co-workers [5a].

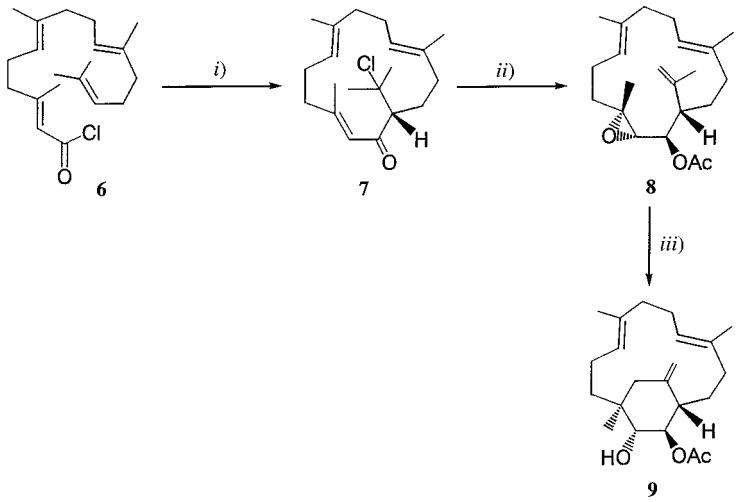
Scheme 1. *Possible Biogenesis of Trinervitane and Kempane Skeletons*



geranylgeranoic acid chloride **6**. As illustrated in *Scheme 2*, the construction of the 14-membered-ring chloro ketone **7** [8] (see also [1]) corresponds to the biogenetic-type transformation of geranylgeranyl-OPP **1** to the neocembrene, while the synthesis of racemic hydroxy acetate **9** from epoxy acetate **8** [9] represents the simulation of the biogenetic-type transformation of the neocembrene **2** to the secotrinervitatriene skeleton in *Scheme 1*.

We have further continued our efforts to explore the synthetic route to the trinervitane and kempane skeletons featuring the biogenesis and succeeded in the construction of both skeletons from the secotrinervitatriene derivative **9**. This paper reports the detailed results of our synthetic study.

Scheme 2. *Biogenetic-Type Synthesis of Secotrinervitatrienediol Acetate* **9**



i) $SnCl_4$, CH_2Cl_2, $-78°$; 72%. *ii*) 1) Li_2CO_3, LiBr, DMF, 105°; 2) DIBAL-H, $-78°$; 3) ^{t}BuOOH, $[VO(acac)_2]$, PhH; 4) Ac_2O, pyridine, DMAP (*N,N*-dimethylpyridin-4-amine), CH_2Cl_2. *iii*) $BF_3 \cdot Et_2O$, $-20°$; 82%.

17-Chloro-7,16-secotrinervita-7,11,15-triene-2,3-diol 30. – Our synthetic study started from the isomerization of the exocyclic C=C bond of hydroxy acetate **9** to the endocyclic isomers **10** and **11** with simultaneous introduction of the functional group at C(17) (*Scheme 3*). We envisioned two different approaches for the construction of the trinervitane skeleton, one being *Lewis* acid promoted cyclization of the conjugated aldehyde **10** to the tricyclic diene carboxaldehyde **12**, while the dechlorinative ring closure of allyl chloride **11** to the triene derivative **13** constitutes an alternative approach. Regarding the position of the newly introduced C=C bond of the expected products **12** and **13**, our preliminary MM2 calculation suggested that the tetrasubstituted isomer possessing the C=C bond between C(7) and C(8) is energetically the most favorable of the three possible isomers. In the case of **13**, the molecular energy of the tetrasubstituted $\Delta^{7,8}$-isomer is 38.9 kcal/mol, while those of the exocyclic $\Delta^{8,19}$-isomer and of the $\Delta^{8,9}$-isomer are 44.7 and 49.7 kcal/mol, respectively[4]). The higher molecular energy of the last two isomers is attributable to the presence of the remaining C=C bond at the 11,12 position. It is noteworthy that all the trinervitane-type natural products lack the C(11)=C(12) bond; they have the unsaturation at the 8,19 or 8,9 position in addition to the 1,15 position.

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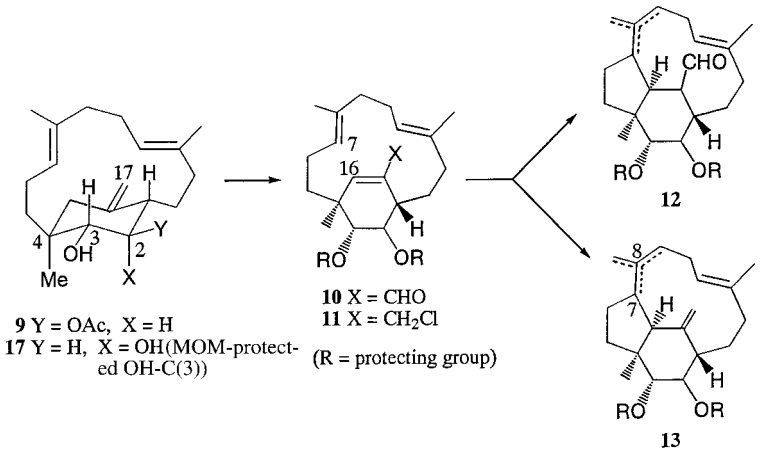
[4]) The CambridgeSoft loaded in *CS ChemOffice* was used for the calculations.

Scheme 3. *The Approach to Construct the Trinervitane Skeletons*



The requisite key intermediates **10** and **11** were prepared from hydroxy acetate **9** as shown in *Schemes 4* and *5*. The 3α-OH group of **9** was protected with chloro(methoxy)methane (MOMCl) to give MOMO acetate **14**, which was hydrolyzed with 2M KOH in MeOH to give the MOMO-protected 2β-OH derivative **15**. Treatment of **15** under *Sharpless* epoxidation conditions with [$VO(acac)_2$] and ^{t}BuOOH resulted in complete recovery of the starting material **15**. The inertness of the epoxidation reaction is explained by the fact that the exocyclic C(15)=C(17) bond of **15** is located too far away from the 2β-equatorial OH group since it is evident from the ^{1}H-NMR spectrum that the cyclohexane ring of **9** exists as chair-like conformation as shown in *Scheme 3* (axial H_α–C(2) at 4.55 (*dd*, *J*(1,2) = 11.9 Hz) and axial H_β–C(3) at 3.65 (*d*, *J*(2,3) = 8.5 Hz)). Regioselective epoxidation is reasonably expected when the *Sharpless* epoxidation would be applied to 2α-OH derivative **17**, an isomer of **9** (see *Scheme 3*). Thus, the hydroxy MOMO-protected 2β-OH derivative **15** was allowed to react with pyridinium chlorochromate (PCC) in the presence of NaOAc, affording the 3-MOMO-protected 2-ketone **16**. Reduction of **16** with $NaBH_4$ at $-15°$ proceeded stereoselectively to provide the 2α-OH isomer **17** exclusively. The high stereoselectivity of the reduction may be caused by the existence of the 4α-axial Me group. The α-axial configuration of the 2-OH group of **17** was confirmed by the ^{1}H-NMR spectrum (small *J*(2,3) of 4.0 Hz). *Sharpless* epoxidation of **17** with anhydrous *tert*-butyl hydroperoxide (^{t}BuOOH) [10] proceeded uneventfully in the presence of $Ti(O^iPr)_4$ to deliver the corresponding epoxy alcohol **18** as a single product.

The ring opening of the epoxide was first examined by the reaction of **18** with lithium isopropylcyclohexylamide (LICA) in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in refluxing THF [5]), affording the expected allyl alcohol, *i.e.*, **20** with 2-OH instead of 2-OMOM, in 54% yield. However, the yield of the reaction was irreproducible on scaling up and also on subtle changes in the reaction conditions, decreasing largely with concomitant decomposition of the starting material.

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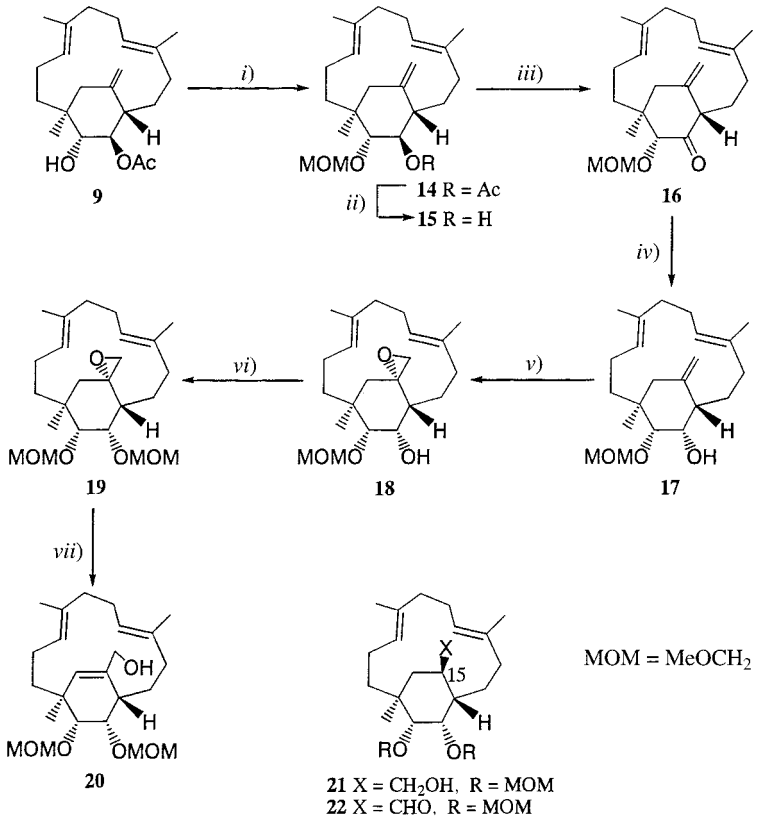
[5]) Ring opening of epoxides with magnesium isopropylcyclohexylamide (MICA) was reported [11].

Scheme 4. *Conversion of Secotrinervitatrienediol Acetate* **9** *to the Synthetic Intermediates*

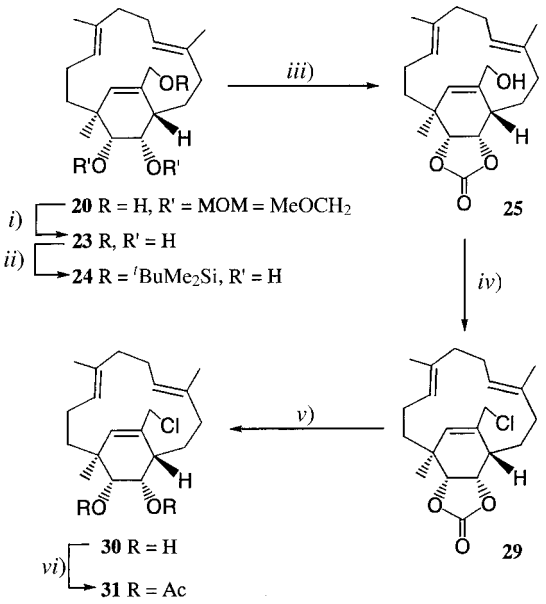


i) MOMCl, $^{i}Pr_2NEt$, CH_2Cl_2; 94%. *ii*) 2N KOH/MeOH; 99%. *iii*) PCC, 4 Å molecular sieves, NaOAc, CH_2Cl_2; 90%. *iv*) $NaBH_4$, MeOH, −15°; 92%. *v*) ^{t}BuOOH, $Ti(O^{i}Pr)_4$, CH_2Cl_2, 0°; 63%, conversion yield; 86%. *vi*) MOMCl, $^{i}Pr_2NEt$, CH_2Cl_2; 94%. *vii*) $Al(O^{i}Pr)_3$, toluene, 105°; 66%.

Alternatively, if the epoxide-ring opening was undertaken with $Al(O^{i}Pr)_3$, after MOM-protection of the 2α-OH group of **18** (→**19**), reproducible yields could be obtained, affording a 1:1 mixture of **19** and **20**. Separation of the mixture, followed by retreatment of the recovered material, provided the allyl alcohol **20** in a practical yield. The major by-product of this reaction was the partly saturated alcohol **21**, presumably formed by reduction [12] of the corresponding aldehyde **22**, a minute by-product of the reaction of **19**. The configuration at C(15) of the partly saturated alcohol **21** was determined unequivocally by X-ray crystallographic analysis, and it played an essential role in the elaboration of the conformation of the macrocyclic structure.

Removal of two MOM groups from **20** with 2M HCl in MeOH to deliver triol **23**, followed by selective protection of the primary OH group with the $^{t}BuMe_2Si$ group furnished diol **24**. After protection of the vicinal secondary OH groups as a carbonate, the protecting $^{t}BuMe_2Si$ group was removed to give the hydroxy carbonate **25** (*Scheme 5*).

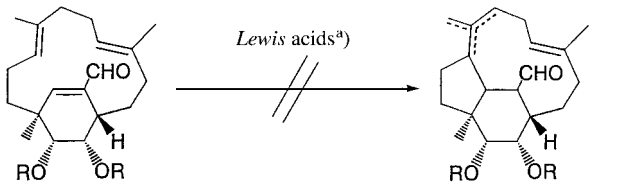
Scheme 5. *Preparation of Allyl Chloride* **30**



i) 2N HCl/MeOH; 90%. *ii*) ^{t}BuMe$_2$SiCl, 1*H*-imidazole, DMF; 90%. *iii*) 1) *N*,*N*′-carbonylbis[1*H*-imidazole] (CDI), PhH; 92%; 2) Bu_4NF, THF; 99%. *iv*) MsCl, Et_3N, LiCl, CH_2Cl_2; 94%. *v*) aq. KOH, $MeOCH_2CH_2OMe$; 98%. *vi*) Ac_2O, pyridine, DMAP; 100%.

By the action of active MnO_2, the MOM-3-protected allyl alcohol corresponding to **20** and the allyl alcohol **25** were easily transformed into the corresponding conjugated aldehydes **26** and **27** (*Scheme 6*). However, submission of both compounds to the ring-closure reaction by the action of a *Lewis* acid such as $BF \cdot OEt_2$, $SnCl_4$, or $EtAlCl_2$ failed to yield any cyclized product at $-78°$ to room temperature. It is noteworthy that the reaction of **27** resulted in the formation of the expected product **28**, but this labile compound was completely decomposed during isolation work.

Scheme 6. *Attempt to Construct the Trinervitane Skeleton*



26 R = MOM
27 R,R = CO

28, R = protecting groups

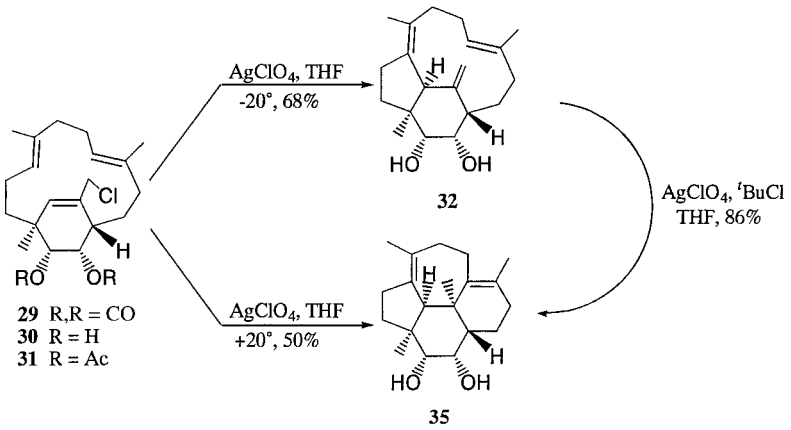
[a]) *Lewis* acids: $SnCl_4$, $BF_3 \cdot OEt_2$, or $EtAlCl_2$.

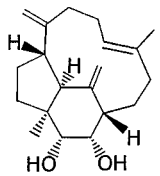
Alternatively, the dechlorinating ring closure was attempted starting from allyl chlorides **30** and **31**, which were prepared from **25** as shown in *Scheme 5*. The hydroxy carbonate **25** was transformed into the corresponding chloro carbonate **29** in 94% yield by the action of methane sulfonyl chloride (MsCl) in the presence of Et_3N, LiCl, and

[12]crown-4. The alkaline hydrolysis of **29** provided chloro diol **30** in high yield, which was acetylated quantitatively under the usual conditions to the chloro diacetate **31**.

Construction of the Trinervitane and Kempane Skeletons. – We eventually found that the desired tricyclic trinervitatriendiols **32** and **33** were isolated in 68 and 5% yields, respectively, besides etheric alcohols **34** as minor products, when chlorodiol **30** was submitted to the reaction with $AgClO_4$ in THF at $-20°$ (*Scheme 7*). It was accidentally found that this ring-closure reaction depends largely on the reaction temperature, *i.e.*, a completely different product was formed when the reaction of **30** with $AgClO_4$ was carried out at $+20°$, affording directly the tetracyclic kempadienediol **35** in 50% yield, after a simple recrystallization. The kempadiene skeleton may be formed from the trinervitatrienediol **32** by protonation at the C(17) methylene group, followed by further ring closure and deprotonation. In fact, treatment of **32** at room temperature with $HClO_4$ in THF, prepared *in situ* by the reaction of *tert*-butyl chloride and $AgClO_4$, gave the kempadienediol **35** in high yield. The formation of the epoxy by-products **34** was avoided when the chloro diacetate **31** instead of chlorodiol **30** was treated with $AgClO_4$ at 25°, giving a 6 : 1 mixture of the diacetates corresponding to **32** and **33** in 95% yield, with no detectable amount of the etheric by-products. The carbonate **29** afforded no cyclization products **32** or **35** under these conditions, leading

Scheme 7. *The Construction of Trinervitane and Kempane Skeletons*





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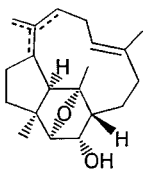


34

to decomposition of the products, in accordance with the already-observed labile nature of carbonate **28** (*Scheme 6*). On a large scale, it was more effective to run the cyclization of triol **23** (*Scheme 5*) instead of that of **30** with $AgClO_4$ in the presence of *tert*-butyl chloride, providing the requisite kempadiene compound **35** in *ca.* 50% yield after purification by a simple recrystallization.

The structure of the cyclized products described so far was established by the detailed study of ^{1}H- and ^{13}C-NMR spectra including NOESY and COSY experiments. The results are summarized in *Tables 1* and *2*. The trinervitatriene skeleton was confirmed by X-ray crystallographic analysis of a derivative[6]) obtained from **32**, while the tetracyclic kempadiene skeleton **35** was supported by its ^{1}H-NMR data (2 tertiary Me at 1.30 and 1.34 ppm, 2 vinyl Me at 1.52 and 1.57 ppm, no olef. H). The configuration at the stereogenic centers C(4), C(15), and C(16) of **35** was demonstrated unequivocally by NOEs (NOEs H–C(16)/Me(17) and Me(18); no NOE of H–C(16), Me(17), and Me(18) with H–C(1), H–C(2), and H–C(3); clear NOEs between H–C(1), H–C(2), and H–C(3)). It is noteworthy that the newly formed stereogenic centers C(15) and C(16) of the kempane skeleton were derived from the bicyclic intermediates **23** and **30**.

Table 1. *^{1}H-NMR Spectra* ($CDCl_3$, 500 MHz) *of* **36**[a]), **32**, *and* **35**. δ in ppm, J in Hz.

	36[b])	**32**	**35**
H–C(1)	2.61 (br. *d*, *J* = 12.5)	2.20 (br. *d*, *J* = 9.0)	1.48–1.54 (*m*)
H–C(2)	4.07 (br. *s*)	3.75 (br. *s*)	3.87 (*dd*, *J* = 2.0, 4.0)
H–C(3)	4.35 (*d*, *J* = 2.5)	3.40 (*d*, *J* = 3.0)	3.46 (br. *s*)
CH_2(5)	1.33 (*ddd*, *J* = 2.0, 5.8, 14.0);	1.09 (*dt*, *J* = 9.0, 11.5);	1.15 (*ddd*, *J* = 4.0, 8.5, 12.5);
	1.89–2.06 (*m*)	1.99–2.02 (*m*)	1.88 (*dd*, *J* = 6.5, 12.5)
CH_2(6)	1.89–2.06 (*m*);	2.37–2.43 (*m*)	2.20–2.30 (*m*)
	2.35 (*dddd*, *J* = 2.0, 9.8, 12.8, 15.9)		
H–C(7)	5.35 (br. *d*, *J* = 9.8)		
CH_2(9)	2.06–2.20 (*m*);	1.69 (br. *d*, *J* = 12.5); 2.53	2.04–2.19 (*m*);
	2.28 (br. *d*, *J* = 13.8)	(*dt*, *J* = 4.0, 12.5)	2.20–2.30 (*m*)
CH_2(10)	1.89–2.06 (*m*);	1.99–2.02 (*m*); 2.16	2.20–2.30 (*m*);
	2.51 (*dddd*, *J* = 4.1, 11.3, 12.6, 14.5)	(*tdd*, *J* = 4.0, 11.0, 12.0)	2.40 (*dt*, *J* = 4.0, 13.4)
H–C(11)	4.68 (br. *d*, *J* = 11.3)	4.99 (*dd*, *J* = 5.5, 11.0)	
CH_2(13)	2.06–2.20 (*m*)	1.88 (*dt*, *J* = 4.5, 12.5);	1.94–2.04 (*m*);
		2.14 (*ddd*, *J* = 3.0, 3.5, 12.5)	2.04–2.19 (*m*)
CH_2(14)	1.54 (*tdd*, *J* = 3.7, 12.5, 13.2);	1.45 (*ddd*, *J* = 3.0, 4.5, 13.5);	1.48–1.55 (*m*);
	1.85 (*dddd*, *J* = 1.9, 5.2, 11.5, 13.2)	1.94 (*ddt*, *J* = 3.5, 9.0, 13.0)	2.04–2.19 (*m*)
H–C(16)	5.45 (*d*, *J* = 3.1)	2.94 (br. *s*)	2.93 (br. *s*)
CH_2(17)	4.07 (*d*, *J* = 10.7); 4.12 (*d*, *J* = 10.7)	4.93 (*s*); 5.06 (*s*)	1.30 (*s*)
or Me(17)			
Me(18)	1.08 (*s*)	0.99 (*s*)	1.34 (*s*)
Me(19)	1.46 (*s*)	1.64 (*s*)	1.52 (*s*)
Me(20)	1.70 (*s*)	1.54 (*s*)	1.57 (*s*)

[a]) **36** is MOM-protected **30** (see below). [b]) Signals of the two MOM groups: 4.56 (*d*, *J* = 6.7, 1 H), 4.92 (*d*, *J* = 6.7, 1 H), and 3.37 (*s*, 3 H) for 2-MOM, and 4.67 (*d*, *J* = 7.0, 1 H), 4.84 (*d*, *J* = 7.0, 1 H), and 3.50 (*s*, 3 H), for 3-MOM.

6) The conversion of **32** to the naturally occurring compounds is in progress.

Table 2. *^{13}C-NMR Spectra* ($CDCl_3$, 125 MHz) *of* **36**[a]), **32**, *and* **35**. δ in ppm.

	36[b])	**32**	**35**
H–C(1)	35.8 (*d*)	44.0 (*d*)	40.5 (*d*)
H–C(2)	71.8 (*d*)	78.3 (*d*)	76.4 (*d*)
H–C(3)	78.2 (*d*)	72.8 (*d*)	72.6 (*d*)
C(4)	42.0 (*s*)	50.7 (*s*)	47.2 (*s*)
CH_2(5)	39.2 (*t*)	37.3 (*t*)	38.6 (*t*)
CH_2(6)	25.2 (*t*)	30.6 (*t*)	30.9 (*t*)
H–C(7)	128.4 (*d*)	136.1 (*s*)	135.5 (*s*)
C(8)	133.8 (*s*)	129.4 (*s*)	126.2 (*s*)
CH_2(9)	38.8 (*t*)	32.9 (*t*)	37.7 (*t*)
CH_2(10)	25.5 (*t*)	24.2 (*t*)	23.9 (*t*)
H–C(11)	127.8 (*d*)	125.8 (*d*)	140.6 (*s*)
C(12)	133.2 (*s*)	132.7 (*s*)	122.1 (*s*)
CH_2(13)	36.1 (*t*)	40.1 (*t*)	31.4 (*t*)
CH_2(14)	20.4 (*t*)	25.9 (*t*)	23.2 (*t*)
C(15)	134.0 (*s*)	148.4 (*s*)	43.1 (*s*)
H–C(16)	138.2 (*d*)	61.1 (*d*)	57.3 (*d*)
CH_2(17) or Me(17)	48.0 (*t*)	112.5 (*t*)	24.9 (*q*)
Me(18)	25.0 (*q*)	21.6 (*q*)	25.1 (*q*)
Me(19)	14.5 (*q*)	18.7 (*q*)	22.4 (*q*)
Me(20)	16.1 (*q*)	15.6 (*q*)	18.8 (*q*)

[a]) **36** is MOM-protected **30** (see below). [b]) Signals of the two MOM groups: 97.2 (*t*) and 55.7 (*q*) for 2-MOM, and 95.3 (*t*) and 55.7 (*q*) for 3-MOM.

Conformational Analysis. – It is of special interest to estimate the probable transition state in the cyclization reaction from the stable conformation of the chloro diol **30**. Concerning the gross structure of **30**, there exist several possible conformations such as **A**, **B**, and **C** (*Fig. 1*), depending on the location of the macrocycle appended at C(1) and C(4) of the cyclohexene ring. The macrocycle of conformer **B** roughly bisects the cyclohexene ring (bisecting conformation), while it is bent to the C(15)=C(16) or C(2)–C(3) bond in the conformers **A** and **C** (bent conformations), respectively. Presuming from the *Dreiding* model that Cl–C(17) is located opposite to the macrocycle, the MM2 force-field calculation was carried out, showing that the bisecting conformation **B** has the lowest energy of 22.84 kcal/mol, while the minimum energies of the bent conformations **A** and **C** are 27.14 and 29.10 kcal/mol, respectively. Thus, the *Dreiding* model and the MM2 calculation suggest that the bisecting conformation is the most favorable one. Since it is crucial that **30** adopts the bent conformation **A** to allow the connection between C(7) and C(16) we propose to explain the experimental evidence concerning the easiness of the five-membered ring formation by the presumption that an indefinite bent conformation may be involved in the transition state reached from the bisecting conformation **B** of the lowest energy level.

The ^{1}H-NMR spectra of chloro diol **30** at 25° and −50° were sharp and almost identical. This evidence as well as the appearance of two olefinic protons as a broad *d*, irrespective of the existence of the vicinal CH_2 group, suggest that the chlorodiol **30** possesses a fixed conformation and that an equilibrium among the conformations **A**–**C** is quite unlikely. If we assume that the chloro diol **30** adopts the bent conformation **A**,

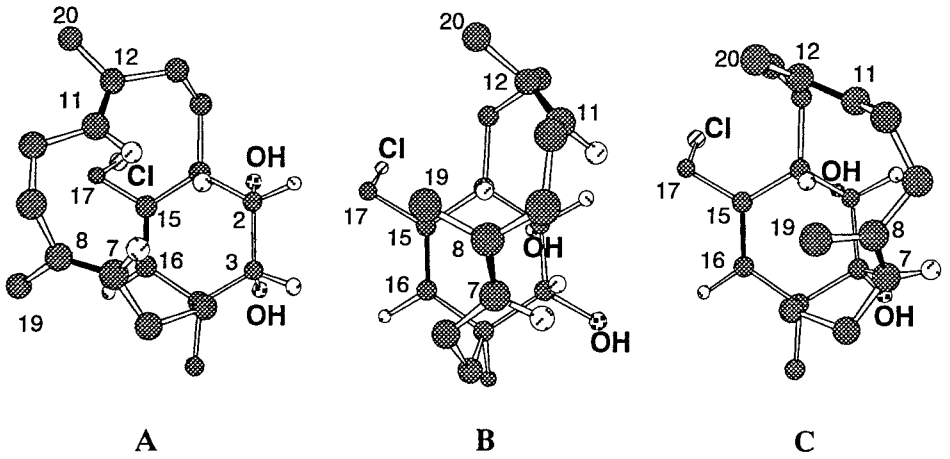
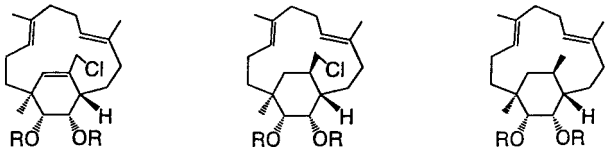


Fig. 1. *Computer-generated perspective drawings of the possible conformations of chlorodiol* **30**. Some H-atoms are omitted

although this is in contradiction to the result from the MM2 calculation, the proximity of the reacting centers at C(7) and C(16) of conformer **A** ought to cause upfield shifts of H–C(7) and/or the Me(19) group by the shielding effect of C(15)=C(16) bond located below H–C(7) and/or Me(19). The chemical shifts of the olefinic protons and the Me groups attached at the C=C bonds of allyl chlorides **30** and **36** (obtained from **20**; see *Exper. Part*) clearly demonstrate that one olefinic proton and one Me group appear at higher field than the remaining signals (*Table 3*). If these upfield shifted signals arise from H–C(7) and Me(19), the bent conformation **A** might be the most probable. To confirm this probability, we compared the chemical shifts of **30** and **36** with those of the partly saturated chlorides **37** (obtained from **21**, see *Exper. Part*) and **38** (*Table 3*). The upfield shift of one olefinic proton is still observed for **37** and **38** although the olefinic Me signals appear in the normal region. This suggests that the



30 R = H
36 R = MOM

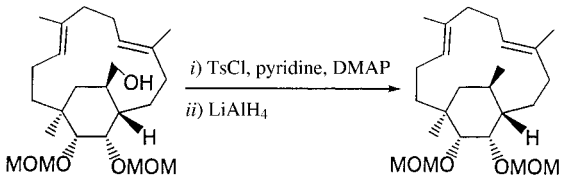
38 R = H
37 R = MOM

39 R = MOM

Table 3. *^{1}H-NMR Chemical Shifts* (500 MHz, $CDCl_3$) *of Olefinic Protons and Methyl Groups*

Compound	H–C=C	Me–C=C (Me(19), Me(20))
30	*4.74*, 5.23, 5.57	*1.43*, 1.68
36	*4.69*, 5.35, 5.45	*1.46*, 1.70
38	*4.74*, 5.20, –	*1.61*, 1.62
37	*4.71*, 5.37, –	*1.60*, 1.62
39	*4.73*, 5.37, –	*1.55* (6H)

Scheme 8



21 **39**

upfield shift of the olefinic proton is not caused by the C(15)=C(16) bond if the Cl-atom at C(17) of the partly saturated chlorides **37** and **38** has no influence on the chemical shift. This is unlikely since the upfield shift of the olefinic proton is still observed in the ^{1}H-NMR spectrum of the dechlorinated derivative **39** (*Table 3*), which was prepared from **21** according to *Scheme 8*.

The definitive evidence was obtained from X-ray and ^{1}H-NMR analyses of the allyl chloride **36**, of which a single crystal suitable for the X-ray measurement was prepared. The X-ray analysis demonstrated that **36** possesses the bisecting conformation **B** (*Fig. 2*). To our surprise, Cl–C(17) protrudes perpendicularly toward the macrocycle. The detailed HMBC, C,H COSY, and NOESY experiments suggest that **36** adopts the same bisecting conformation also in the ^{1}H-NMR solution, in which the Cl-atom exists at the same site with respect to the macrocycle without free rotation around the C(15)–C(17) bond. Thus, clear NOEs are observed between H–C(7) (δ 5.35 (d, $J = 9.8$ Hz)) and H–C(3) (δ 4.35 (d, $J = 2.5$ Hz)). In addition, the CH_2(17) protons of **36** are nonequivalent (δ 4.07 (d, $J = 10.7$ Hz) and 4.12 (d, $J = 10.7$ Hz)), one of them (δ 4.07) exhibiting an NOE with H–C(16), while the latter correlates with one proton of CH_2(14). The conformation of the allyl chloride **36** shown in *Fig. 2* illustrates clearly

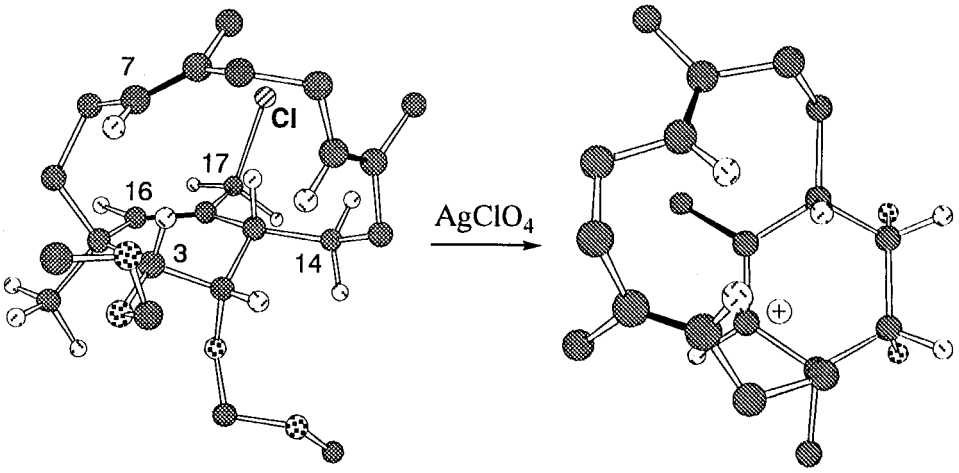


Fig. 2. *Computer-generated perspective drawing of the X-ray model of* **36** *and the bent conformation of the allyl cation intermediate.* Some H-atoms are omitted for clarity perspective drawing of the X-ray model of **36** bent conformation of the allyl-cation intermediate (MOM groups are omitted).

that the upfield-shifted signals of the olefinic proton at δ 4.68 and the olefinic Me group at δ 1.46 have to be assigned to H–C(11) and Me(19), respectively; in this conformation, the olfinic proton suffers the shielding of the C(7)=C(8) bond, while the olefinic Me group is affected by the C(15)=C(16) bond.

The evidence descibed so far indicates that the starting allyl chloride **30** exists in the bisecting conformation, from which an allyl cation is formed by the action of $AgClO_4$. The change from the bisecting conformation **B** to the bent conformation **A** might occur at the allyl-cation intermediate as shown in *Fig. 2*, and this change is crucial for the facilitation of the five-membered-ring formation, leading to the trinervitatriene skeletons **32** and **33**. The C(7) and C(16) diastereofaces of the allyl-cation intermediate are disposed to deliver H–C(7) of **33** in the β-configuration (7β-H). The C(7) configuration of all the naturally occurring trinervitanes, more than three dozens of which have been accumulated from various kinds of termite soldiers, has been assigned as being 7α (7α-H) without any exception. This opposite configuration at C(7) of **33** suggests that the conformation of the secotrinervitatriene intermediate in the biosynthesis of the trinervitane natural products is different from those disclosed in the present study. The difference may be due to the participation of the C(11)=C(12) and C(1)=C(15) bonds. As illustrated in *Scheme 1*, the H-shift from C(1) to C(12) of secotrinervitatriene seems to be a crucial step in the biosynthesis, resulting in the migration of the C(15)=C(16) bond to the 1,15 position. The subsequent construction of the five-membered ring possessing α-configuration at C(7) (7α-H) seems to be the most probable in the biosynthesis.

We are grateful to Professor *K. Sakai* of the Science University of Tokyo for his kind guidance on the X-ray crystallographic analyses.

Experimental Part

General. The descriptor (±) is omitted from the names of the racemic compounds. Reactions were conducted under N_2 or Ar when anh. solvents were used. Tetrahydrofuran (THF), Et_2O, and hexane for the reaction solvents were distilled from sodium-benzophenone ketyl. Distilled Et_2O and AcOEt were used for extraction. Anal. TLC: aluminium sheets coated with silica gel *60 F_{254}*, AcOEt/hexane mixtures; visualization with UV light and then staining with 0.5% anisaldehyde in 2M aq. H_2SO_4. CC (column chromatography): silica gel *60* (Art. 7734, 70–230 mesh); FC = medium-pressure flash chromatography. M.p.: *Yanako HP* apparatus; uncorrected. IR Spectra: films on NaCl windows or KBr pellets; *Hitachi 270-30* spectrophotometer. ^{1}H- and ^{13}C-NMR Spectra: $CDCl_3$ solns. with $SiMe_4$ as an internal standard, *JEOL* spectrometers; δ in ppm, J in Hz; assignments are based on the reference compounds **36** (= **30** with R = MOM), **32**, and **35** in *Tables 1* and *2*; the purity of all the oil derivatives were confirmed by ^{13}C-NMR. MS: *Hitachi M-80B* spectrometer. Combustion analyses: *Yanaco MT-6* CHN recorder.

7,16-Secotrinervita-7,11,15(17)-triene-2β,3α-diol 2-Acetate (= *(1*RS*,12*RS*,13*SR*,14*SR*)-1,5,9-Trimethyl-16-methylidenebicyclo[10.2.2]hexadeca-4,8-diene-13,14-diol 13-Acetate*; **9**). $BF_3 \cdot Et_2O$ (0.082 ml, 0.67 mmol) was added dropwise to a soln. of 2-acetoxy-3-epoxyneocembrene **8** (116 mg, 0.33 mmol) [9a] in Et_2O (3 ml) at –20°. The mixture was stirred at –20° for 48 h. After the addition of sat. aq. $NaHCO_3$ soln. (3 ml), the mixture was extracted with Et_2O (3 × 15 ml), the org. phase washed with sat. aq. $NaHCO_3$ soln. (2 × 7 ml) and brine (3 × 7 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 10:1): 95 mg (82%) of **9**. Colorless needles. M.p. 78–79° (hexane). IR (CCl_4): 3700–3300, 2956, 1744, 1656, 1374, 1240, 1024, 894. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86 (*s*, Me(18)); 1.25–1.35 (*m*, H–C(5), H–C(14)); 1.46 (*tdd*, J = 3.7, 11.9, 14.7, H–C(14)); 1.56 (*s*, Me(20)); 1.61 (*s*, Me(19)); 1.70 (*d*, J = 13.1, H–C(16)); 1.76 (*td*, J = 4.3, 14.0, H–C(5)); 1.79–1.84 (br. *d*, J = 5.2, OH); 1.97–2.09 (*m*, H–C(6), H–C(10), 2 H–C(13)); 2.12 (*s*, Ac); 2.16–2.24 (*m*, H–C(9)); 2.20 (*t*, J = 11.9, H–C(1)); 2.35 (br. *d*, J = 14.1, H–C(9)); 2.43–2.54 (*m*, H–C(6), H–C(10)); 2.89 (*d*, J = 13.1, H–C(16)); 3.65 (*dd*, J = 5.2, 8.5, H–C(3)); 4.55 (*dd*, J = 8.5, 11.9, H–C(2)); 4.74

(*s*, H–C(17)); 4.77 (br. *d*, *J* = 9.8, H–C(11)); 4.82 (*s*, H–C(17)); 5.24 (br. *d*, *J* = 10.4, H–C(7)). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.3 (*q*, C(19)); 15.0 (*q*, C(20)); 19.6 (*t*, C(14)); 21.1 (*q*, C(18)); 21.9 (*q*, MeCO); 25.1 (*t*, C(6)); 25.2 (*t*, C(10)); 36.5 (*t*, C(13)); 36.6 (*t*, C(5)); 39.3 (*s*, C(4)); 39.7 (*t*, C(9)); 42.7 (*d*, C(1)); 46.9 (*t*, C(16)); 75.7 (*d*, C(3)); 77.4 (*d*, C(2)); 107.4 (*t*, C(17)); 127.4 (*d*, C(7)); 128.3 (*d*, C(11)); 132.9 (*s*, C(8)); 133.5 (*s*, C(12)); 144.3 (*s*, C(15)); 171.6 (*s*, Me*CO*). Anal. calc. for $C_{22}H_{34}O_3$: C 76.26, H 9.89; found: C 76.28, H 9.94.

3α-(Methoxymethoxy)-7,16-secotrinervita-7,11,15(17)-trien-2β-ol Acetate (=*(1*RS,*12*RS,*13*SR,*14*SR*)-14-(Methoxymethoxy)-1,5,9-trimethyl-16-methylidenebicyclo[10.2.2]hexadeca-4,8-dien-13-ol Acetate*; **14**). A mixture of **9** (96 mg, 0.27 mmol), ^{i}Pr$_2$NEt (0.48 ml, 2.76 mmol), $ClCH_2OMe$ (0.11 ml, 1.45 mmol) and CH_2Cl_2 (7 ml) was stirred at 20° for 20 h. After the addition of H_2O (5 ml) and sat. aq. NH_4Cl soln. (5 ml), the mixture was extracted with Et_2O (3 × 15 ml), the org. phase washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 8:1): 102 mg (94%) of **14**. Colorless prisms. M.p. 110–111° (hexane). IR (CCl_4): 2932, 1742, 1236, 1036. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.91 (*s*, Me(18)); 1.24 (*dddd*, *J* = 2.2, 4.0, 12.0, 14.4, H–C(14)); 1.29 (*ddd*, *J* = 4.0, 11.9, 14.4, H–C(5)); 1.47 (*tdd*, *J* = 3.7, 11.6, 14.4, H–C(14)); 1.56 (*s*, Me(20)); 1.64 (*s*, Me(19)); 1.69 (*d*, *J* = 13.5, H–C(16)); 1.75 (*td*, *J* = 4.0, 14.4, H–C(5)); 1.95–2.06 (*m*, H–C(6), H–C(10), 2 H–C(13)); 2.08 (*s*, Ac); 2.15 (*t*, *J* = 11.6, H–C(1)); 2.19 (*ddd*, *J* = 3.4, 12.8, 14.1, H–C(9)); 2.33 (br. *d*, *J* = 14.1, H–C(9)); 2.49 (*dddd*, *J* = 3.4, 10.7, 12.8, 15.0, H–C(10)); 2.70 (*dddd*, *J* = 4.0, 11.3, 11.9, 15.0, H–C(6)); 2.92 (*d*, *J* = 13.5, H–C(16)); 3.37 (*s*, *Me*OCH$_2$); 3.59 (*d*, *J* = 7.9, H–C(3)); 4.64 (*d*, *J* = 6.7, MeOC*H*$_2$); 4.68 (*dd*, *J* = 7.9, 11.6, H–C(2)); 4.72 (*d*, *J* = 1.3, H–C(17)); 4.77 (*d*, *J* = 10.7, H–C(11)); 4.81 (*s*, H–C(17)); 4.91 (*d*, *J* = 6.7, MeOC*H*$_2$O); 5.26 (*dd*, *J* = 3.7, 11.3, H–C(7)). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.5 (*q*, C(19)); 14.9 (*q*, C(20)); 20.1 (*t*, C(14)); 21.2 (*q*, *Me*CO); 23.5 (*q*, C(18)); 24.5 (*t*, C(6)); 25.2 (*t*, C(10)); 36.4 (*t*, C(13)); 37.0 (*t*, C(5)); 39.56 (*s*, C(4)); 39.59 (*t*, C(9)); 42.4 (*d*, C(1)); 46.5 (*t*, C(16)); 55.7 (*q*, *Me*OCH$_2$); 77.4 (*d*, C(2)); 82.9 (*d*, C(3)); 97.7 (*t*, MeO*C*H$_2$O); 107.2 (*t*, C(17)); 127.3 (*d*, C(7)); 128.2 (*d*, C(11)); 133.0 (*s*, C(8)); 133.4 (*s*, C(12)); 144.1 (*s*, C(15)); 170.3 (*s*, Me*C*O). HR-MS: 390.2739 ($C_{24}H_{38}O_4^+$; calc. 390.2771). Anal. calc. for $C_{24}H_{38}O_4$: C 73.81, H 9.81; found: C 73.61, H 9.42.

3α-(Methoxymethoxy)-7,16-secotrinervita-7,11,15(17)-trien-2β-ol (=*(1*RS,*12*RS,*13*SR,*14*SR*)-14-(Methoxymethoxy)-1,5,9-trimethyl-16-methylidenebicyclo[10.2.2]hexadeca-4,8-dien-13-ol*; **15**). A soln. of **14** (48 mg, 0.12 mmol) in 2M KOH/MeOH (4 ml) was stirred at 20° for 48 h. After the addition of H_2O (5 ml), the mixture was extracted with Et_2O (3 × 20 ml), the org. phase washed with brine (2 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 8:1): 43 mg (99%) of **15**. Colorless prisms. M.p. 85–86° (hexane). IR (CCl_4): 3464, 2916, 1654, 1452, 1378, 1150, 1106, 1036, 888. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.85 (*s*, Me(18)); 1.26 (*ddd*, *J* = 4.3, 12.5, 14.1, H–C(5)); 1.43 (*tdd*, *J* = 3.7, 11.6, 13.5, H–C(14)); 1.60 (*s*, Me(20)); 1.62 (*s*, Me(19)); 1.63 (*d*, *J* = 14.0, H–C(16)); 1.68 (*td*, *J* = 4.3, 14.1, H–C(5)); 1.87 (*dddd*, *J* = 2.2, 7.5, 9.5, 13.5, H–C(14)); 1.96 (*t*, *J* = 11.6, H–C(1)); 2.00–2.08 (*m*, H–C(6), H–C(10), 2 H–C(13)); 2.19 (*ddd*, *J* = 3.7, 12.8, 14.4, H–C(9)); 2.33 (br. *d*, *J* = 14.4, H–C(9)); 2.41 (*dddd*, *J* = 4.3, 11.3, 12.5, 15.3, H–C(6)); 2.50 (*dddd*, *J* = 3.7, 11.0, 12.8, 14.8, H–C(10)); 2.97 (br. *d*, *J* = 14.0, H–C(16)); 3.20 (*dd*, *J* = 8.3, 11.6, H–C(2)); 3.32 (*d*, *J* = 8.3, H–C(3)); 3.44 (*s*, *Me*OCH$_2$O); 4.04 (*s*, OH); 4.67 (*d*, *J* = 1.3, H–C(17)); 4.74 (*s*, H–C(17)); 4.75 (*d*, *J* = 11.0, H–C(11)); 4.82 (*s*, MeOC*H*$_2$O); 5.22 (*d*, *J* = 11.3, H–C(7)). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.4 (*q*, C(19)); 15.3 (*q*, C(20)); 18.9 (*t*, C(14)); 23.2 (*q*, C(18)); 25.1 (*t*, C(10)); 25.4 (*t*, C(6)); 36.7 (*t*, C(13)); 36.8 (*t*, C(5)); 39.7 (*s*, C(4)); 39.8 (*t*, C(9)); 44.2 (*d*, C(1)); 47.8 (*t*, C(16)); 55.6 (*q*, *Me*OCH$_2$O); 73.0 (*d*, C(2)); 90.0 (*d*, C(3)); 98.4 (*t*, MeO*C*H$_2$O); 105.9 (*t*, C(17)); 127.0 (*d*, C(7)); 127.4 (*d*, C(11)); 132.9 (*s*, C(8)); 134.5 (*s*, C(12)); 145.8 (*s*, C(15)). HR-MS: 348.2662 ($C_{22}H_{36}O_3^+$; calc. 348.2666). Anal. calc. for $C_{22}H_{36}O_3$: C 75.82, H 10.41; found: C 75.94, H 10.57.

3α-(Methoxymethoxy)-7,16-secotrinervita-7,11,15(17)-trien-2-one (=*(1*RS,*12*RS,*14*SR*)-14-(Methoxymethoxy)-1,5,9-trimethyl-16-methylidenebicyclo[10.2.2]hexadeca-4,8-dien-13-one*; **16**). A soln. of **15** (180 mg, 0.52 mmol) in CH_2Cl_2 (2 ml) was added to a vigorously stirred mixture of pyridinium chlorochromate (366 mg, 1.70 mmol), NaOAc (635 mg, 7.74 mmol), and 4 Å molecular sieves (366 mg) in CH_2Cl_2 (6 ml) at 20°. After vigorous stirring at 20° for 4 h, Et_2O (20 ml) was added, the mixture passed through a pad of SiO_2 (8 g), the pad washed with Et_2O (5 × 8 ml), the combined filtrate evaporated, and the residue purified by CC (hexane/AcOEt 10:1): 161 mg (90%) of **16**. Colorless prisms. M.p. 93–95° (hexane). IR (CCl_4): 2924, 1736, 1154, 1106, 1030, 910. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.83 (*s*, Me(18)); 1.35 (*ddd*, *J* = 4.3, 6.1, 14.6, H–C(5)); 1.43 (*dddd*, *J* = 3.4, 4.6, 10.4, 13.7, H–C(14)); 1.55 (*s*, Me(20)); 1.64 (*s*, Me(19)); 1.85 (*ddd*, *J* = 3.7, 10.4, 14.1, H–C(13)); 1.87 (*d*, *J* = 13.5, H–C(16)); 1.94 (*dddd*, *J* = 3.7, 7.4, 8.1, 13.7, H–C(14)); 1.97 (*ddd*, *J* = 4.3, 10.4, 14.6, H–C(5)); 2.07 (*ddd*, *J* = 3.4, 7.4, 14.1, H–C(13)); 2.17 (br. *d*, *J* = 13.4, H–C(10)); 2.25–2.35 (*m*, H–C(6), 2 H–C(9), H–C(10)); 2.51 (*dddd*, *J* = 4.3, 8.3, 10.4, 14.5, H–C(6)); 2.92 (br. *d*, *J* = 13.5, H–C(16)); 3.24 (*dd*, *J* = 4.6, 8.1, H–C(1)); 3.48 (*s*, *Me*OCH$_2$O); 4.69 (*s*, H–C(17)); 4.69 (*d*, *J* = 7.0, MeOC*H*$_2$); 4.70 (br. *d*, *J* = 6.1, H–C(11)); 4.74 (*d*, *J* = 7.0, MeOC*H*$_2$); 4.79 (*s*, H–C(17)); 4.84 (*s*, H–C(3)); 5.44 (*dd*, *J* = 7.2, 8.3, H–C(7)). ^{13}C-NMR

(100 MHz, $CDCl_3$): 14.1 (*q*, C(19)); 15.3 (*q*, C(20)); 18.5 (*t*, C(14)); 22.7 (*q*, C(18)); 25.1 (*t*, C(6)); 25.3 (*t*, C(10)); 34.8 (*t*, C(5)); 36.8 (*t*, C(13)); 39.5 (*t*, C(9)); 42.6 (*s*, C(4)); 45.4 (*t*, C(16)); 53.4 (*d*, C(1)); 56.1 (*q*, *Me*OCH_2O); 83.3 (*d*, C(3)); 96.4 (*t*, MeO*C*H_2O); 108.4 (*t*, C(17)); 126.6 (*d*, C(7)); 128.1 (*d*, C(11)); 134.0 (*s*, C(8)); 134.1 (*s*, C(12)); 144.5 (*s*, C(15)); 206.5 (*s*, C(2)). HR-MS: 346.2501 ($C_{22}H_{34}O_3^+$; calc. 346.2509). Anal. calc. for $C_{22}H_{34}O_3$: C 76.26, H 9.89; found: C 76.14, H 10.07.

3α-(Methoxymethoxy)-7,16-secotrinervita-7,11,15(17)-trien-2α-ol (*=(1*RS*,12*RS*,13*RS*,14*SR*)-14-(Methoxymethoxy)-1,5,9-trimethyl-16-methylidenebicyclo[10.2.2]hexadeca-4,8-dien-13-ol*; **17**). $NaBH_4$ (24 mg, 0.64 mmol) was added to a stirred soln. of **16** (110 mg, 0.32 mmol) in MeOH (3 ml) at −15°. After stirring at −15° for 4 h, H_2O (5 ml) was added, the mixture extracted with Et_2O (3 × 15 ml), the combined org. layer was washed with brine (2 × 3 ml, twice), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 5:1): 102 mg (92%) of **17**. Colorless oil. IR (CCl_4): 3592, 2940, 1658, 1440, 1357, 1214, 1152, 1096, 1038. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.96 (*s*, Me(18)); 1.17 (*ddd*, *J* = 4.3, 9.5, 14.3, H−C(5)); 1.39 (*tdd*, *J* = 5.5, 8.0, 14.1, H−C(14)); 1.57 (*s*, Me(19), Me(20)); 1.61 (*d*, *J* = 6.4, OH); 1.71 (*tdd*, *J* = 5.8, 7.6, 14.1, H−C(14)); 1.73 (*d*, *J* = 13.1, H−C(16)); 1.80 (*ddd*, *J* = 4.0, 7.3, 14.3, H−C(5)); 2.00–2.08 (*m*, 2 H−C(13)); 2.15–2.35 (*m*, H−C(1), H−C(6), 2 H−C(9), 2 H−C(10)); 2.40 (*dddd*, *J* = 4.0, 8.0, 9.5, 14.3, H−C(6)); 2.73 (*d*, *J* = 13.1, H−C(16)); 3.47 (*s*, *Me*OCH_2O); 3.77 (*d*, *J* = 4.0, H−C(3)); 3.92 (*t*, *J* = 4.0, H−C(2)); 4.72 (*d*, *J* = 7.0, MeO*C*H_2O); 4.75 (*d*, *J* = 1.3, H−C(17)); 4.76 (br. *t*, *J* = 6.1, H−C(11)); 4.87 (*d*, *J* = 7.0, MeO*C*H_2O); 4.96 (*s*, H−C(17)); 5.27 (br. *t*, *J* = 8.0, H−C(7)). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.0 (*q*, C(19)); 15.3 (*q*, C(20)); 23.1 (*t*, C(14)); 24.7 (*q*, C(18)); 25.1 (*t*, C(6), C(10)); 36.5 (*t*, C(13)); 37.5 (*t*, C(5)); 39.5 (*t*, C(9)); 40.0 (*s*, C(4)); 42.2 (*d*, C(1)); 46.4 (*t*, C(16)); 55.7 (*q*, *Me*OCH_2O); 72.0 (*d*, C(2)); 78.8 (*d*, C(3)); 95.2 (*t*, MeO*C*H_2O); 108.4 (*t*, C(17)); 127.2 (*d*, C(7)); 127.9 (*d*, C(11)); 132.8 (*s*, C(8)); 133.6 (*s*, C(12)); 144.8 (*s*, C(15)). HR-MS: 348.2673 ($C_{22}H_{36}O_3^+$; calc. 348.2666).

15,17-Epoxy-3α-(methoxymethoxy)-7,16-secotrinervita-7,11-dien-2α-ol (*=(1*RS*,12*SR*,13*SR*,15*SR*,16*RS*)-15-(Methoxymethoxy)-1,5,9-trimethylspiro[bicyclo[10.2.2]hexadeca-4,8-diene-13,2′-oxiran]-16-ol*; **18**). Under N_2, $Ti(O^iPr)_4$ (0.36 ml, 1.22 mmol) was added, to a soln. of **17** (426 mg, 1.22 mmol) in CH_2Cl_2 (15 ml) at 0°. After stirring at 0° for 5 min, anh. 2M ^{t}BuOOH/CH_2ClCH_2Cl (3.1 ml, 6.11 mmol) was added and the mixture was stirred at 0° for 39 h. The mixture was poured into sat. aq. $NaHCO_3$ soln. (0.5 ml), then passed through a pad of SiO_2 (8 g), the pad washed with CH_2Cl_2 (4 × 15 ml), the combined org. extract evaporated, and the residue purified by CC (hexane/AcOEt 10:1): 279 mg (63%) of **18** and 115 mg (27%) of **17**, **18**. Colorless prisms. M.p. 79–81° (hexane). IR (CCl_4): 3576, 2932, 1450, 1388, 1098, 1040. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.10 (*d*, *J* = 14.2, H−C(16)); 1.18 (*s*, Me(18)); 1.20–1.28 (*m*, H−C(5), H−C(14)); 1.33 (*dddd*, *J* = 4.3, 6.0, 9.3, 14.4, H−C(14)); 1.55 (*s*, Me(20)); 1.58 (*s*, Me(19)); 1.77 (*ddd*, *J* = 4.2, 7.1, 14.4, H−C(5)); 1.92 (*ddd*, *J* = 4.1, 9.3, 13.6, H−C(13)); 2.00 (*dd*, *J* = 6.0, 6.7, H−C(1)); 2.12 (*ddd*, *J* = 4.3, 7.4, 13.6, H−C(13)); 2.14–2.30 (*m*, 2 H−C(6), 2 H−C(9), 2 H−C(10)); 2.38 (*d*, *J* = 14.2, H−C(16)); 2.41 (*d*, *J* = 4.2, H−C(17)); 2.65 (*d*, *J* = 4.2, H−C(17)); 2.76 (*d*, *J* = 6.4, OH); 3.49 (*s*, *Me*OCH_2O); 3.76 (*d*, *J* = 4.0, H−C(3)); 4.04 (*ddd*, *J* = 2.2, 4.0, 6.4, H−C(2)); 4.74 (*d*, *J* = 7.0, MeO*C*H_2); 4.79 (br. *t*, *J* = 6.3, H−C(11)); 4.90 (*d*, *J* = 7.0, MeO*C*H_2O; 5.27 (br. *t*, *J* = 7.6, H−C(7)). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.2 (*q*, C(19)); 15.2 (*q*, C(20)); 21.1 (*t*, C(14)); 24.9 (*t*, C(6)); 25.1 (*t*, C(10)); 25.9 (*q*, C(18)); 35.7 (*d*, C(1)); 37.3 (*t*, C(13)); 38.3 (*t*, C(5)); 38.6 (*s*, C(4)); 39.5 (*t*, C(9)); 43.9 (*t*, C(16)); 47.1 (*t*, C(17)); 55.7 (*q*, *Me*OCH_2O); 58.7 (*s*, C(15)); 73.0 (*d*, C(2)); 78.3 (*d*, C(3)); 95.1 (*t*, MeO*C*H_2O); 126.7 (*d*, C(7)); 128.9 (*d*, C(11)); 132.8 (*s*, C(8)); 133.3 (*s*, C(12)). HR-MS: 364.2583 ($C_{22}H_{36}O_4^+$; calc. 364.2615). Anal. calc. for $C_{22}H_{36}O_4$: C 72.49, H 9.95; found: C 72.44, H 10.15.

15,17-Epoxy-2α,3α-bis(methoxymethoxy)-7,16-secotrinervita-7,11-diene (*=(1*RS*,12*SR*,13*SR*,15*SR*,16*RS*)-15,16-Bis(methoxymethoxy)-1,5,9-trimethylspiro[bicyclo[10.2.2]hexadeca-4,8-dien-13,2′-oxirane]*; **19**). Under N_2, a mixture of **18** (260 mg, 0.71 mmol), ^{i}Pr$_2$NEt (1.24 ml, 7.13 mmol), and $ClCH_2OMe$ (0.27 ml, 3.57 mmol) in CH_2Cl_2 (10 ml) was stirred at 20° for 22 h. After the addition of sat. aq. NH_4Cl soln. (5 ml) and H_2O (5 ml), the mixture was extracted with Et_2O (3 × 15 ml). The combined org. phase washed with brine (2 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 8:1): 273 mg (94%) of **19**. Colorless prisms. M.p. 79–81° (hexane). IR (CCl_4): 2932, 1152, 1096, 1034, 918. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.16 (*s*, Me(18)); 1.17 (*dddd*, *J* = 4.6, 6.7, 8.0, 14.3, H−C(14)); 1.18–1.33 (*m*, H−C(5), H−C(14)); 1.32 (*d*, *J* = 14.4, H−C(16)); 1.55 (*s*, Me(19), Me(20)); 1.76 (*ddd*, *J* = 3.7, 7.6, 14.4, H−C(5)); 1.93–1.99 (*m*, H−C(1), H−C(13)); 2.06 (*ddd*, *J* = 3.7, 8.0, 12.6, H−C(13)); 2.10–2.35 (*m*, H−C(6), 2 H−C(9), 2 H−C(10)); 2.18 (*d*, *J* = 14.4, H−C(16)); 2.33 (*d*, *J* = 4.6, H−C(17)); 2.39–2.46 (*m*, H−C(6)); 2.53 (*d*, *J* = 4.6, H−C(17)); 3.38 (*s*, *Me*O-CH_2O); 3.46 (*s*, *Me*OCH_2O); 3.81 (*d*, *J* = 3.0, H−C(3)); 3.96 (br. *d*, *J* = 3.0, H−C(2)); 4.63 (*d*, *J* = 7.0, MeO*C*H_2O); 4.64 (*d*, *J* = 7.1, MeO*C*H_2O); 4.77 (br. *t*, *J* = 6.7, H−C(11)); 4.80 (*d*, *J* = 7.0, MeO*C*H_2O); 4.88 (*d*, *J* = 7.1, MeO*C*H_2O); 5.31 (br. *t*, *J* = 7.1, H−C(7)). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.2, (*q*, C(19)); 15.3, (*q*, C(20)); 21.3 (*t*, C(14)); 24.8 (*t*, C(6)); 25.2 (*t*, C(10)); 25.7 (*q*, C(18)); 36.4 (*d*, C(1)); 37.4 (*t*, C(13)); 38.5 (*s*, C(4)); 39.0 (*t*, C(5)); 39.4 (*t*, C(9)); 44.6 (*t*, C(16)); 47.7 (*t*, C(17)); 55.4 (*q*, *Me*OCH_2O); 55.7 (*q*, *Me*OCH_2);

57.1 (*s*, C(15)); 76.4 (*d*, C(2)); 78.4 (*d*, C(3)); 94.7 (*t*, MeO*C*H$_2$); 96.9 (*t*, MeO*C*H$_2$); 127.1 (*d*, C(7)); 128.7 (*d*, C(11)); 132.8 (*s*, C(8)); 133.3 (*s*, C(12)). HR-MS: 408.2876 ($C_{24}H_{40}O_5^+$; calc. 408.2877). Anal. calc. for $C_{24}H_{40}O_5$: C 70.55, H 9.87; found: C 70.55, H 10.26.

3α-(Methoxymethoxy)-7,16-secotrinervita-7,11,15-triene-2α,17-diol (= *(1*RS*,12*RS*,15*SR*,16*RS*)-16-Hydroxy-15-(methoxymethoxy)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8,13-triene-13-methanol*; **20** (2-OH instead of 2-OMOM)). Under Ar, 1.55M BuLi hexane (2.4 ml, 3.7 mmol) was added to stirred isopropylcyclohexylamine (0.53 ml, 3.7 mmol) soln. in THF (30 ml) at −78°. After stirring at −78° for 30 min and at 0° for 30 min, tetramethylethylenediamine (TMEDA) (0.43 ml, 3.7 mmol) and then **18** (194 mg, 0.5 mmol) in THF (3 ml) were added dropwise. After the mixture was refluxed for 2 h, sat. aq. NH_4Cl soln. (15 ml) and then brine (30 ml) were added at 0°. After extraction with AcOEt (3 × 20 ml), the org. layer was washed with brine (3 × 10 ml), dried (Na_2SO_4), and evaporated. The residue was purified by CC (hexane/AcOEt 2:1): 105 mg (54%) of **20** (2-OH instead of 2-OMOM). M.p. 132–133° (hexane). IR (CCl_4): 3400, 2932, 1450, 1388, 1260, 1154, 1104, 1034. ^{1}H-NMR (90 MHz, $CDCl_3$): 1.12 (*s*, Me(18)); 1.39 (*s*, Me(19)); 1.64 (*s*, Me(20)); 3.50 (*s*, *Me*OCH$_2$O); 3.84–4.20 (*m*, H–C(2), H–C(3), 2 H–C(17)); 4.60–4.80 (*m*, H–C(11)); 4.72, 4.86 (2*d*, *J* = 7.5, MeOC*H*$_2$O); 5.10–5.40 (*m*, H–C(7)); 5.34 (br. *s*,H–C(16)). ^{13}C-NMR (22.5 MHz, $CDCl_3$): 13.9 (*q*, C(19)); 15.7 (*q*, C(20)); 20.8 (*t*, C(14)); 25.3 (*q*, C(18)); 25.6 (*t*, C(6)); 26.3 (*t*, C(10)); 36.5 (*t*, C(13)); 36.8 (*d*, C(1)); 38.8 (*t*, C(9)); 39.7 (*t*, C(5)); 41.0 (*s*, C(4)); 55.6 (*q*, *Me*OCH$_2$O); 65.0 (*t*, C(17)); 67.9 (*d*, C(2)); 79.1 (*d*, C(3)); 95.9 (*t*, MeO*C*H$_2$O); 127.9 (*d*, C(11)); 128.5 (*d*, C(7)); 133.0 (*s*, C(12)); 133.6 (*d*, C(16)); 134.0 (*s*, C(8)); 135.5 (*s*, C(15)). HR-MS: 364.2609 ($C_{22}H_{36}O_4^+$; calc. 364.2615). Anal. calc. for $C_{22}H_{36}O_4$: C 72.49, H 9.95; found: C 72.55, H 10.26.

2α,3α-Bis(methoxymethoxy)-7,16-secotrinervita-7,11,15-trien-17-ol (= *(1*RS*,12*RS*,15*SR*,16*RS*)-15,16-Bis(methoxymethoxy)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8,13-triene-13-methanol*; **20**). A soln. of **19** (418 mg, 1.02 mmol) and Al(O^{i}Pr)$_3$ (209 mg, 1.02 mmol) in toluene (13 ml) was kept at 105° for 18 h. Then H_2O (10 ml) was added at 10° and the mixture extracted with Et_2O (3 × 10 ml). The combined org. extract was washed with brine (3 × 10 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 8:1): 169 mg of recovered **19** and *2α,3α-bis(methoxymethoxy)-7,16-secotrinervita-7,11-dien-17-ol* (= *(1*RS*,12*RS*,13*SR*,15*SR*,16*RS*)-15,16-Bis(methoxymethoxy)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8-diene-13-methanol*; **21**) as an inseparable mixture, 12 mg of *2α,3α-bis(methoxymethoxy)-7,16-secotrinervita-7,11-dien-17-al* (= *(1*RS*,12*RS*,13*SR*,15*SR*,16*RS*)-15,16-Bis(methoxymethoxy)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8-diene-13-carbaldehyde*; **22**), and then 201 mg (48%) of **20**. The inseparable mixture **19**/**21** (169 mg) was treated again with Al(O^{i}Pr)$_3$ (84 mg) in toluene (6 ml) at 105° for 15 h, and the mixture was separated by CC. Repetition of this reaction three times provided **20** (276 mg, 66%), **21** (67 mg, 16%), and **22** (46 mg, 11%).

Data of **20**: Colorless prisms. M.p. 124–126° (hexane). IR (CCl_4): 3620, 2932, 1450, 1386, 1214, 1154, 1110, 1040, 918. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.09 (*s*, Me(18)); 1.30 (*ddd*, *J* = 2.2, 5.8, 14.1, H–C(5)); 1.43 (*s*, Me(19)); 1.57 (*tdd*, *J* = 3.7, 11.9, 13.8, H–C(14)); 1.64 (*s*, Me(20)); 1.71 (*dddd*, *J* = 2.0, 3.9, 12.0, 13.8, H–C(14)); 1.88–2.18 (*m*, H–C(5), H–C(6), H–C(9), H–C(10), 2 H–C(13)); 2.23–2.37 (*m*, H–C(6), H–C(9)); 2.46 (*dddd*, *J* = 4.4, 10.6, 12.0, 14.4, H–C(10)); 2.53 (br. *d*, *J* = 11.9, H–C(1)); 3.37 (*s*, *Me*OCH$_2$O); 3.50 (*s*, *Me*OCH$_2$O); 4.03 (*dd*, *J* = 1.7, 2.2, H–C(2)); 4.07 (*s*, 2 H–C(17)); 4.24 (*d*, *J* = 2.2, H–C(3)); 4.57 (*d*, *J* = 7.0, MeOC*H*$_2$O); 4.66 (*d*, *J* = 6.7, MeOC*H*$_2$O); 4.67–4.69 (br. *d*, *J* = 10.6, H–C(11)); 4.84 (*d*, *J* = 7.0, MeOC*H*$_2$O); 4.94 (*d*, *J* = 6.7, MeOC*H*$_2$O); 5.28 (*d*, *J* = 3.1, H–C(16)); 5.34 (br. *d*, *J* = 10.4, H–C(7)). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.8 (*q*, C(19)); 15.8 (*q*, C(20)); 20.8 (*t*, C(14)); 25.1 (*q*, C(18)); 25.3 (*t*, C(6)); 25.5 (*t*, C(10)); 36.3 (*t*, C(13)); 36.5 (*d*, C(1)); 38.8 (*t*, C(9)); 39.0 (*t*, C(5)); 41.4 (*s*, C(4)); 55.7 (*q*, *Me*OCH$_2$O); 55.8 (*q*, *Me*OCH$_2$O); 65.2 (*t*, C(17)); 72.0 (*d*, C(2)); 78.9 (*d*, C(3)); 95.4 (*t*, MeO*C*H$_2$O); 97.1 (*t*, MeO*C*H$_2$O); 127.9 (*d*, C(11)); 128.7 (*d*, C(7)); 133.1 (*s*, C(12)); 133.2 (*s*, C(8)); 133.5 (*d*, C(16)); 136.1 (*s*, C(15)). HR-MS: 408.2876 $C_{24}H_{40}O_5^+$; calc. 408.2877). Anal. calc. for $C_{24}H_{40}O_5$: C 70.55, H 9.87; found: C 70.59, H 10.19.

Data of **21**: Colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.02 (*td*, *J* = 4.2, 14.2, H–C(5)); 1.06 (*s*, Me(18)); 1.21 (*t*, *J* = 11.7, H–C(1)); 1.27 (*dd*, *J* = 3.0, 12.7, H–C(16)); 1.29 (*tdd*, *J* = 4.0, 11.7, 12.7, H–C(14)); 1.50 (*ddt*, *J* = 2.0, 4.6, 12.7, H–C(14)); 1.49 (*t*, *J* = 12.7, H–C(16)); 1.56 (*s*, Me(19)); 1.58 (*s*, Me(20)); 1.63 (br. *s*, OH); 1.97 (*ddd*, *J* = 4.4, 12.0, 14.2, H–C(5)); 1.98–2.05 (*m*, H–C(6), H–C(10), H–C(13), H–C(15)); 2.10 (*dt*, *J* = 4.0, 12.7, H–C(13)); 2.19 (*ddd*, *J* = 3.4, 12.7, 14.4, H–C(9)); 2.31 (br. *d*, *J* = 14.4, H–C(9)); 2.47 (*dddd*, *J* = 3.2, 10.2, 12.7, 14.8, H–C(10)); 2.49 (*dddd*, *J* = 4.2, 11.0, 12.0, 14.5, H–C(6)); 3.37 (*s*, *Me*OCH$_2$O); 3.47 (*dd*, *J* = 5.8, 10.7, H–C(17)); 3.49 (*s*, *Me*OCH$_2$O); 3.64 (*dd*, *J* = 4.2, 10.7, H–C(17)); 3.89 (*d*, *J* = 3.7, H–C(2)); 3.96 (*d*, *J* = 3.7, H–C(3)); 4.59 (*d*, *J* = 6.6, MeOC*H*$_2$O); 4.65 (*d*, *J* = 6.8, MeOC*H*$_2$O); 4.74 (br. *d*, *J* = 10.2, H–C(11)); 4.80 (*d*, *J* = 6.6, MeOC*H*$_2$O); 4.84 (*d*, *J* = 6.8, MeOC*H*$_2$O); 5.37 (br. *d*, *J* = 11.0, H–C(7)). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.1 (*q*, C(19)); 15.4 (*q*, C(20)); 21.1 (*t*, C(14)); 24.8 (*q*, C(18)); 25.2 (*t*, C(6)); 25.3 (*t*, C(10)); 32.3 (*d*, C(15)); 36.2 (*t*, C(5)); 36.4 (*t*, C(13)); 38.1 (*s*, C(4)); 39.2 (*d*, C(1)); 39.3 (*t*, C(16)); 39.6 (*t*, C(9)); 55.4 (*q*, *Me*OCH$_2$O); 55.8 (*q*, *Me*OCH$_2$O); 65.7 (*t*, C(17)); 73.4 (*d*, C(2)); 79.6 (*d*, C(3)); 95.4 (*t*, MeO*C*H$_2$O); 97.4

(*t*, MeO*C*H$_2$O); 127.1 (*d*, C(7)); 127.8 (*d*, C(11)); 132.4 (*s*, C(8)); 133.4 (*s*, C(12)). HR-MS: 410.3037 ($C_{24}H_{42}O_5^+$; calc. 410.3032).

Data of **22**: Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.06 (*s*, Me(18)); 1.07 (*td*, *J* = 4.0, 14.4, H–C(5)); 1.23 (*dd*, *J* = 4.0, 13.0, H–C(16)); 1.27 (*dddd*, *J* = 2.2, 4.4, 11.8, 13.9, H–C(14)); 1.43 (*tdd*, *J* = 4.2, 11.0, 13.9, H–C(14)); 1.57 (*s*, Me(19)); 1.59 (*s*, Me(20)); 1.65 (*ddd*, *J* = 2.2, 11.0, 11.5, H–C(1)); 1.77 (*dd*, *J* = 12.0, 13.0, H–C(16)); 1.98 (*ddd*, *J* = 4.4, 12.0, 14.4, H–C(5)); 2.00–2.10 (*m*, H–C(6), H–C(10), H–C(13)); 2.08 (*ddd*, *J* = 4.2, 11.8, 12.8, H–C(13)); 2.21 (*ddd*, *J* = 3.4, 11.0, 13.5, H–C(9)); 2.33 (br. *d*, *J* = 13.5, H–C(9)); 2.45 (*dtd*, *J* = 3.7, 11.0, 15.2, H–C(10)); 2.48 (*dddd*, *J* = 4.0, 10.7, 12.0, 14.4, H–C(6)); 2.81 (*tdd*, *J* = 4.0, 11.5, 12.0, H–C(15)); 3.37 (*s*, *Me*OCH$_2$O); 3.47 (*s*, *Me*OCH$_2$O); 3.88 (*d*, *J* = 3.2, H–C(2)); 3.96 (*d*, *J* = 3.2, H–C(3)); 4.58 (*d*, *J* = 6.6, MeOC*H*$_2$O); 4.64 (*d*, *J* = 6.8, MeOC*H*$_2$O); 4.75 (br. *d*, *J* = 11.0, H–C(11)); 4.81 (*d*, *J* = 6.6, MeOC*H*$_2$O); 4.84 (*d*, *J* = 6.8, MeOC*H*$_2$O); 5.38 (br. *d*, *J* = 10.7, H–C(7)); 9.50 (*d*, *J* = 4.0, H–C(17)). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.1 (*q*, C(19)); 15.4 (*q*, C(20)); 22.9 (*t*, C(14)); 24.6 (*q*, C(18)); 25.2 (*t*, C(6)); 25.3 (*t*, C(10)); 35.5 (*t*, C(5)); 36.1 (*t*, C(13)); 36.4 (*t*, C(16)); 37.7 (*s*, C(4)); 38.1 (*d*, C(1)); 39.6 (*t*, C(9)); 44.8 (*d*, C(15)); 55.6 (*q*, *Me*OCH$_2$O); 56.0 (*q*, *Me*OCH$_2$O); 72.8 (*d*, C(2)); 78.9 (*d*, C(3)); 95.3 (*t*, MeO*C*H$_2$O); 97.4 (*t*, MeO*C*H$_2$O); 126.8 (*d*, C(7)); 128.5 (*d*, C(11)); 132.8 (*s*, C(8)); 133.1 (*s*, C(12)); 205.6 (*d*, C(17)). HR-MS: 408.2871 ($C_{24}H_{40}O_5^+$; calc. 408.2876).

2α,3α-Bis(methoxymethoxy)-7,16-secotrinervita-7,11,15-trien-17-al (=*(1*RS,*12*RS,*15*SR,*16*RS*)-15,16-Bis(methoxymethoxy)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8,13-triene-13-carbaldehyde*; **26**). A mixture of **20** (2-OH instead of 2-OMOM) (105 mg, 0.30 mmol) and active MnO_2 (250 mg, 8.7 mmol) in CH_2Cl_2 (10 ml) was refluxed for 6 h. Then the mixture was passed through a pad of SiO_2 (8 g), the pad washed with CH_2Cl_2 (6 × 10 ml), the combined org. extract evaporated, and the residue purified by CC (hexane/AcOEt 5:1): 99 mg (95%) of **26** (2-OH instead of 2-OMOM). M.p. 119–121° (hexane). IR (CCl_4): 2940, 1692, 1450, 1104, 1034. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.24 (*s*, Me(18)); 1.30 (*s*, Me(19)); 1.70 (*s*, Me(20)); 3.50 (*s*, *Me*OCH$_2$O); 4.05 (*s*, H–C(2)); 4.16 (*d*, *J* = 2.6, H–C(3)); 4.65 (*d*, *J* = 11.5, H–C(11)); 4.72, 4.82 (2*d*, *J* = 6.9, MeOC*H*$_2$O); 5.22 (*d*, *J* = 9.2, H–C(7)); 6.29 (*d*, *J* = 3.0, H–C(16)); 9.53 (*s*, H–C(17)). ^{13}C-NMR (22.5 MHz, $CDCl_3$): 13.8 (*q*, C(19)); 15.8 (*q*, C(20)); 18.7 (*t*, C(14)); 25.1 (*q*, C(18)); 25.1 (*t*, C(6)); 25.7 (*t*, C(10)); 35.3 (*d*, C(1)); 36.8 (*t*, C(5)); 39.1 (*t*, C(13)); 39.6 (*t*, C(9)); 42.4 (*s*, C(4)); 55.7 (*q*, *Me*OCH$_2$O); 67.9 (*d*, C(2)); 78.5 (*d*, C(3)); 96.0 (*t*, MeO*C*H$_2$O); 127.2 (*d*, C(7)); 127.6 (*d*, C(11)); 134.0 (*s*, C(8)); 134.7 (*s*, C(12)); 138.9 (*s*, C(15)); 160.9 (*d*, C(16)); 193.9 (*d*, C(17)). HR-MS: 362.2444 ($C_{22}H_{34}O_4^+$; calc. 362.2458). Anal. calc. for $C_{22}H_{34}O_4$: C 72.89, H 9.45; found: C 72.59, H 9.19.

A soln. of **26** (2-OH instead of 2-OMOM) (35 mg, 0.097 mmol), ^{i}Pr$_2$NEt (0.1 ml, 0.58 mmol), and ClCH$_2$OMe (22 µl, 0.23 mmol) in CH_2Cl_2 (3 ml) was refluxed for 20 h. After the addition of CH_2Cl_2 (7 ml) and sat. aq. NH_4Cl soln. (3 ml) at 20°, the org. phase was washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated and the residue purified by CC (hexane/AcOEt 4:1): 38 mg (90%) of **26**. White powder. ^{1}H-NMR (90 MHz, $CDCl_3$): 1.22 (*s*, Me(18)); 1.30 (*s*, Me(19)); 1.70 (*s*, Me(20)); 3.37, 3.50 (2*s*, *Me*OCH$_2$O); 4.01–4.10 (*m*, H–C(2)); 4.28 (*d*, *J* = 2.6, H–C(3)); 4.50–4.80 (*m*, H–C(11)); 4.59, 4.64, 4.80, 4.96 (4*d*, *J* = 7.2, MeOC*H*$_2$O); 5.20–5.38 (*m*, H–C(7)); 6.28 (*d*, *J* = 2.8, H–C(16)); 9.53 (*s*, H–C(17)). HR-MS: 406.2744 ($C_{24}H_{38}O_5^+$; calc. 406.2719).

2α,3α-Dihydroxy-7,16-secotrinervita-7,11,15-trien-17-al 2α,3α-Carbonate (=*(3a*RS,*4*RS,*7*RS,*7α*SR*)-3α,4,7,7a-Tetrahydro-7,11,15-trimethyl-2-oxo-4,7-deca[3,7]dieno-1,3-benzodioxol-5-carbaldehyde*; **27**). A mixture of **25** (40 mg, 0.12 mmol) and active MnO_2 (100 mg, 1.20 mmol) in CH_2Cl_2 (5 ml) was refluxed for 4 h and then passed through a pad of SiO_2 (5 g). The pad was washed with CH_2Cl_2 (6 × 10 ml), the combined org. extract evaporated, and the residue purified by CC (hexane/AcOEt 3:1): 34 mg (95%) of **27**. IR (CCl_4): 2924, 1808, 1704, 1366, 1168, 1104, 1072, 1038. ^{1}H-NMR (90 MHz, $CDCl_3$): 1.42 (*s*, Me(18)); 1.50 (*s*, Me(19)); 1.60 (*s*, Me(20)); 4.76 (*dd*, *J* = 1.3, 8.7, H–C(3)); 4.96–5.10 (*m*, H–C(7), H–C(11)); 5.11 (*d*, *J* = 2.6, H–C(2)); 6.66 (br. *s*, H–C(16)); 9.59 (*s*, H–C(17)). ^{13}C-NMR (22.5 MHz, $CDCl_3$): 14.4, (*q*, C(19)); 15.5 (*q*, C(20)); 20.8 (*t*, C(14)); 21.7 (*t*, C(6)); 23.4 (*q*, C(18)); 25.3 (*t*, C(10)); 33.9 (*d*, C(1)); 36.0 (*s*, C(4)); 37.0 (*t*, C(13)); 39.6 (*t*, C(5)); 39.9 (*t*, C(9)); 76.4 (*d*, C(2)); 80.2 (*d*, C(3)); 123.8 (*d*, C(7)); 128.1 (*d*, C(11)); 132.8 (*s*, C(8)); 138.9 (*s*, C(12)); 139.6 (*s*, C(15)); 154.0 (*s*, C=O); 158.3 (*d*, C(16)); 192.3 (*d*, C(17)). HR-MS: 344.1992 ($C_{21}H_{28}O_3^+$; calc. 344.1988).

7,16-Secotrinervita-7,11,15-triene-2α,3α,17-triol (=*(1*RS,*12*RS,*13*RS,*14*SR*)-16-(Hydroxymethyl)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8,15-triene-13,14-diol;* **23**). A soln. of **20** (102 mg, 0.25 mmol) in 2M HCl/MeOH (4 ml) was stirred at 20° for 22 h. After addition of sat. aq. $NaHCO_3$ soln. (15 ml), the mixture was extracted with Et_2O (3 × 10 ml), the combined org. extract washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 2:1): 72 mg (90%) of **23**. Colorless prisms. M.p. 138–140° (hexane). IR (CCl_4): 3592, 2912, 1432, 1384, 1110, 1026, 900. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.06

(*s*, Me(18)); 1.29 – 1.37 (*m*, H–C(5), OH); 1.37 (*s*, Me(19)); 1.45 (br. *d*, *J* = 8.9, OH); 1.55 – 1.73 (*m*, 2 H–C(14)); 1.63 (*s*, Me(20)); 1.92 – 2.16 (*m*, H–C(5), H–C(6), H–C(9), H–C(10), 2 H–C(13)); 2.19 (br. *d*, *J* = 10.4, H–C(9)); 2.22 – 2.33 (*m*, H–C(6), OH); 2.44 (*dddd*, *J* = 4.3, 11.3, 12.5, 14.4, H–C(10)); 2.65 (br. *d*, *J* = 11.6, H–C(1)); 3.86 (br. *d*, *J* = 6.4, H–C(2)); 4.05 – 4.13 (*m*, H–C(3), 2 H–C(17)); 4.74 (br. *d*, *J* = 11.3, H–C(11)); 5.24 (br. *d*, *J* = 10.1, H–C(7)); 5.42 (*d*, *J* = 1.9, H–C(16)). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.8 (*q*, C(19)); 15.6 (*q*, C(20)); 20.9 (*t*, C(14)); 25.2 (*t*, C(6)); 25.5 (*t*, C(10)); 25.9 (*q*, C(18)); 36.4 (*t*, C(13)); 37.0 (*d*, C(1)); 38.6 (*t*, C(9)); 39.8 (*t*, C(5)); 41.2 (*s*, C(4)); 64.8 (*t*, C(17)); 71.0 (*d*, C(2)); 73.3 (*d*, C(3)); 128.1 (*d*, C(11)); 128.2 (*d*, C(7)); 132.7 (*s*, C(12)); 133.7 (*s*, C(8)); 134.8 (*d*, C(16)); 135.4 (*s*, C(15)). HR-MS: 320.2346 ($C_{20}H_{32}O_3^+$; calc. 320.2353). Anal. calc. for $C_{20}H_{32}O_3$: C 74.96, H 10.06; found: C 74.87, H 9.98.

*17-{[(*tert*-Butyl)dimethylsilyl]oxy}-7,16-secotrinervita-7,11,15-triene-2α,3α-diol* (= *(1*RS,*12*RS,*13*RS,*14*SR*)-16-{[(*tert*-Butyl)dimethylsilyl]oxy}methyl}-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8,15-triene-13,14-diol*; **24**). ^{t}BuMe$_2$SiCl (243 mg, 1.61 mmol) was added to a stirred mixture of **23** (261 mg, 0.82 mmol) and 1*H*-imidazole (168 mg, 2.46 mmol) in DMF (7 ml) at 25°. The mixture was stirred for 20 min. Then sat. aq. NH_4Cl soln. (2 ml) and then H_2O (2 ml) were added. The mixture was extracted with Et_2O (3 × 10 ml), the combined org. extract washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 4 : 1): 319 mg (90%) of **24**. Colorless needles. M.p. 72 – 74° (hexane). IR (CCl_4): 3590, 2960, 2860, 1394, 1252, 1050. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.049, 0.053 (2*s*, MeSi); 0.90 (*s*, ^{t}BuSi); 1.02 (*s*, Me(18)); 1.27 (*ddd*, *J* = 2.4, 5.8, 14.9, H–C(5)); 1.34 (*s*, Me(19)); 1.50 – 1.62 (*m*, H–C(14)); 1.59 (*s*, Me(20)); 1.86 – 2.15 (*m*, H–C(5), H–C(6), H–C(9), H–C(10), 2 H–C(13)); 2.20 (br. *d*, *J* = 10.3, H–C(9)); 2.24 (*dddd*, *J* = 2.4, 10.3, 13.0, 15.9, H–C(6)); 2.43 (*dddd*, *J* = 4.3, 10.5, 12.0, 14.4, H–C(10)); 2.58 (br. *d*, *J* = 9.5, H–C(1)); 3.81 (*s*, H–C(2)); 4.02 (*s*, H–C(3), 2 H–C(17)); 4.71 (br. *d*, *J* = 10.5, H–C(11)); 5.21 (br. *d*, *J* = 10.3, H–C(7)); 5.38 (*d*, *J* = 3.0, H–C(16)). ^{13}C-NMR (100 MHz, $CDCl_3$): −5.4, −5.3 (2*q*, MeSi); 14.0 (*q*, C(19)); 15.7 (*q*, C(20)); 18.4 (*s*, Me$_3$*C*Si); 20.3 (*t*, C(14)); 25.2 (*t*, C(6)); 25.4 (*t*, C(10)); 26.0 (*q*, *Me*$_3$CSi); 26.2 (*q*, C(18)); 36.3 (*t*, C(13)); 37.1 (*d*, C(1)); 38.6 (*t*, C(9)); 39.9 (*t*, C(5)); 41.2 (*s*, C(4)); 64.7 (*t*, C(17)); 71.2 (*d*, C(2)); 73.3 (*d*, C(3)); 127.9 (*d*, C(11)); 128.4 (*d*, C(7)); 132.6 (*s*, C(12)); 133.3 (*d*, C(16)); 133.7 (*s*, C(8)); 134.9 (*s*, C(15)). HR-MS: 434.3205 ($C_{26}H_{46}O_3Si^+$; calc. 434.3218).

7,16-Secotrinervita-7,11,15-triene-2α,3α,17-triol 2α,3α-Carbonate (= *(3a*RS,*4*SR,*7*SR,*7a*SR*)-3a,4,7,7a-Tetrahydro-6-(hydroxymethyl)-4,10,14-trimethyl-4,7-deca[3,7]dieno-1,3-benzodioxol-2-one*; **25**). A mixture of **24** (287 mg, 0.66 mmol) and 1,1′-carbonylbis[1*H*-imidazole] (322 mg, 1.98 mmol) in benzene (10 ml) was stirred at 20° for 1 h. Then H_2O (5 ml) and Et_2O (15 ml) were added. The org. phase was dried (Na_2SO_4) and evaporated and the residue purified by CC (hexane/AcOEt 20 : 1): 279 mg (92%) of the 17-(^{t}BuMe$_2$SiO)-substituted 2α,3α-carbonate. Colorless prisms. M.p. 85 – 87° (hexane). IR (CCl_4): 2960, 1808, 1368, 1170, 1070. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.02, 0.04 (*s*, MeSi); 0.87 (*s*, ^{t}BuSi); 1.22 (*s*, Me(18)); 1.29 (*dd*, *J* = 10.7, 14.4, H–C(5)); 1.46 (*s*, Me(20)); 1.54 (*s*, Me(19)); 1.60 (*dd*, *J* = 8.7, 14.4, H–C(5)); 1.73 (*tt*, *J* = 3.4, 12.4, H–C(14)); 1.85 (*ddd*, *J* = 7.4, 10.7, 15.2, H–C(6)); 2.00 – 2.12 (*m*, H–C(1), H–C(6), 2 H–C(9), H–C(10), 2 H–C(13), H–C(14)); 2.38 (*dddd*, *J* = 3.4, 9.2, 11.0, 15.2, H–C(10)); 4.00 (*d*, *J* = 13.2, H–C(17)); 4.18 (*d*, *J* = 13.2, H–C(17)); 4.63 (*dd*, *J* = 1.2, 8.6, H–C(3)); 4.99 (br. *d*, *J* = 9.2, H–C(11)); 5.07 (*dd*, *J* = 3.9, 8.6, H–C(2)); 5.15 (*t*, *J* = 7.4, H–C(7)); 5.58 (br. *s*, H–C(16)). ^{13}C-NMR (100 MHz, $CDCl_3$): −5.4, −5.2 (2*q*, MeSi); 14.2 (*q*, C(19)); 15.2 (*q*, C(20)); 18.1 (*s*, Me$_3$*C*Si); 19.8 (*t*, C(14)); 21.7 (*t*, C(6)); 23.9 (*q*, C(18)); 25.2 (*t*, C(10)); 25.8 (*q*, *Me*$_3$CSi); 33.8 (*d*, C(1)); 35.7 (*t*, C(13)); 37.7 (*t*, C(5)); 37.9 (*s*, C(4)); 39.6 (*t*, C(9)); 64.3 (*t*, C(17)); 76.4 (*d*, C(2)); 80.8 (*d*, C(3)); 124.5 (*d*, C(7)); 127.8 (*d*, C(11)); 131.2 (*d*, C(16)); 132.6 (*s*, C(12)); 137.6 (*s*, C(15)); 138.2 (*s*, C(8)); 154.7 (*s*, C=O). HR-MS: 460.2987 ($C_{27}H_{44}O_4Si^+$; calc. 460.3010). Anal. calc. for $C_{27}H_{44}O_4Si$: C 70.39, H 9.63; found: C 70.35, H 9.83.

To a soln. of the 17-(^{t}BuMe$_2$SiO)-substituted 2α,3α-carbonate (220 mg, 0.48 mmol) in THF (3 ml), 1.0M Bu_4NF in THF (1.43 ml, 1.43 mmol) was added. The mixture was stirred at 25° for 1.5 h, then H_2O (5 ml) was added. The mixture was extracted with Et_2O (3 × 10 ml), the org. phase washed with brine (3 × 4 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 15 : 1): 185 mg (99%) of **25**. M.p. 52 – 55°. IR (CCl_4): 3616, 2920, 1808, 1452, 1370, 1170, 1070, 1038. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.26 (*s*, Me(18)); 1.30 (*dd*, *J* = 11.0, 14.6, H–C(5)); 1.50 (*s*, Me(20)); 1.57 (*s*, Me(19)); 1.64 (*dd*, *J* = 8.8, 14.6, H–C(5)); 1.80 (*tt*, *J* = 3.4, 12.9, H–C(14)); 1.88 (*ddd*, *J* = 7.1, 11.0, 15.6, H–C(6)); 2.00 – 2.12 (*m*, H–C(9), H–C(10), H–C(14), OH–C(17)); 2.15 – 2.30 (*m*, H–C(1), H–C(6), H–C(9), 2 H–C(13)); 2.40 (*dddd*, *J* = 2.5, 9.3, 13.3, 14.9, H–C(10)); 4.08 (*d*, *J* = 14.0, H–C(17)); 4.14 (*d*, *J* = 14.0, H–C(17)); 4.68 (*d*, *J* = 8.6, H–C(3)); 5.02 (br. *d*, *J* = 9.3, H–C(11)); 5.11 (*dd*, *J* = 3.7, 8.6, H–C(2)); 5.17 (*t*, *J* = 7.1, H–C(7)); 5.68 (br. *s*, H–C(16)). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.2 (*q*, C(19)); 15.2 (*q*, C(20)); 20.0 (*t*, C(14)); 21.6 (*t*, C(6)); 23.8 (*q*, C(18)); 25.1 (*t*, C(10)); 33.9 (*d*, C(1)); 35.6 (*t*, C(13)); 37.8 (*t*, C(5)); 37.8 (*s*, C(4)); 39.5 (*t*, C(9)); 63.6 (*t*, C(17)); 76.5 (*d*, C(2)); 80.8 (*d*, C(3)); 124.4 (*d*, C(7)); 127.9 (*d*, C(11)); 132.0 (*d*, C(16)); 132.5 (*s*, C(12)); 137.9 (*s*, C(15));

138.1 (*s*, C(8)); 154.9 (*s*, C=O). HR-MS: 346.2139 ($C_{21}H_{30}O_4^+$; calc. 346.2145). Anal. calc. for $C_{21}H_{30}O_4$: C 72.80, H 8.73; found: C 72.52, H 8.43.

17-Chloro-7,16-secotrinervita-7,11,15-triene-2α,3α-diol Carbonate (=*(3a*RS,*4*SR,*7*SR,*7a*SR*)-6-(Chloromethyl)-3a,4,7,7a-tetrahydro-4,10,14-trimethyl-4,7-deca[3,7]dieno-1,3-benzodioxol-2-one*; **29**). Under N_2, MeSO$_2$Cl (90 µl, 1.17 mmol) was added to a stirred mixture of **25** (270 mg, 0.78 mmol), LiCl (99 mg, 2.34 mmol), and Et_3N (0.22 ml, 1.56 mmol) in CH_2Cl_2 (8 ml) at 0°. After addition of [12]-crown-4 (3 mg), the ice bath was removed and stirring continued at 25° for 17 h. A soln. of sat. aq. NH_4Cl soln. (5 ml) was added, the mixture extracted with Et_2O (3 × 10 ml), the combined org. extract washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 15:1): 268 mg (94%) of **29**. Colorless prisms. M.p. 133–134° (hexane). IR (CCl_4): 2964, 1808, 1368, 1170, 1070, 1038. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.26 (*s*, Me(18)); 1.32 (*dd*, *J* = 10.8, 14.6, H–C(5)); 1.50 (*s*, Me(19)); 1.61 (*s*, Me(20)); 1.66 (*dd*, *J* = 8.5, 14.6, H–C(5)); 1.79 (*tt*, *J* = 4.0, 10.5, H–C(14)); 1.89 (*ddd*, *J* = 7.1, 10.8, 15.9, H–C(6)); 1.90–2.09 (*m*, H–C(9), H–C(10)); 2.17–2.32 (*m*, H–C(1), H–C(6), H–C(9), 2 H–C(13), H–C(14)); 2.44 (*dddd*, *J* = 2.0, 11.2, 13.1, 14.9, H–C(10)); 4.00 (*d*, *J* = 11.0, H–C(17)); 4.14 (*d*, *J* = 11.0, H–C(17)); 4.69 (*dd*, *J* = 1.2, 8.6, H–C(3)); 5.03 (br. *d*, *J* = 11.2, H–C(11)); 5.12 (*dd*, *J* = 3.9, 8.6, H–C(2)); 5.14 (br. *t*, *J* = 7.1, H–C(7)); 5.79 (*s*, H–C(16)). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.2 (*q*, C(19)); 15.4 (*q*, C(20)); 20.0 (*t*, C(14)); 21.7 (*t*, C(6)); 23.9 (*q*, C(18)); 25.2 (*t*, C(10)); 33.3 (*d*, C(1)); 35.6 (*t*, C(13)); 37.9 (*t*, C(5)); 38.2 (*s*, C(4)); 39.6 (*t*, C(9)); 46.5 (*t*, C(17)); 75.9 (*d*, C(2)); 80.5 (*d*, C(3)); 124.2 (*d*, C(7)); 127.8 (*d*, C(11)); 132.7 (*s*, C(12)); 135.3 (*s*, C(15)); 137.2 (*d*, C(16)); 138.7 (*s*, C(8)); 154.5 (*s*, C=O). HR-MS: 364.1802 ($C_{21}H_{29}O_3Cl^+$; calc. 364.1807). Anal. calc. for $C_{21}H_{29}ClO_3$: C 69.12, H 8.01; found C 68.89, H 8.23.

17-Chloro-7,16-secotrinervita-7,11,15-triene-2α,3α-diol (=*(1*RS,*12*RS,*13*RS,*14*SR*)-16-(Chloromethyl)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8,15-triene-13,14-diol*; **30**). To a stirred soln. of chloro-carbonate **29** (55 mg, 0.15 mmol) in $MeOCH_2CH_2OMe$ (3 ml) at 0°, 2M aq. KOH (2 ml) was added. After stirring at 25° for 3 h, the mixture was extracted with Et_2O (3 × 10 ml), the combined org. extract washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 1:1): 50 mg (98%) of **30**. Colorless prisms. M.p. 126–127° (hexane). IR (KBr): 3650–3300, 2956, 2908, 1436, 1254, 1024. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.05 (*s*, Me(18)); 1.36 (*ddd*, *J* = 2.2, 5.8, 13.8, H–C(5)); 1.43 (*s*, Me(19)); 1.61 (*tdd*, *J* = 3.7, 12.5, 13.5, H–C(14)); 1.68 (*s*, Me(20)); 1.80 (*ddt*, *J* = 1.5, 3.5, 13.5, H–C(14)); 1.95–2.17 (*m*, H–C(5), H–C(6), H–C(9), H–C(10), 2 H–C(13)); 2.22–2.34 (*m*, H–C(6), H–C(9)); 2.51 (*dddd*, *J* = 4.0, 11.3, 12.5, 14.4, H–C(10)); 2.69 (br. *d*, *J* = 12.5, H–C(1)); 3.91 (br. *s*, H–C(2)); 4.03 (*d*, *J* = 11.0, H–C(17)); 4.08 (*d*, *J* = 11.0, H–C(17)); 4.15 (*d*, *J* = 2.5, H–C(3)); 4.73 (*d*, *J* = 11.3, H–C(11)); 5.23 (*d*, *J* = 9.5, H–C(7)); 5.56 (*d*, *J* = 2.8, H–C(16)). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.5 (*q*, C(19)); 15.8 (*q*, C(20)); 20.4 (*t*, C(14)); 25.2 (*t*, C(6)); 25.3 (*t*, C(10)); 25.9 (*q*, C(18)); 36.2 (*t*, C(13)); 36.4 (*d*, C(1)); 38.7 (*t*, C(9)); 39.9 (*t*, C(5)); 41.8 (*s*, C(4)); 47.4 (*t*, C(17)); 70.6 (*d*, C(2)); 72.7 (*d*, C(3)); 127.96 (*d*, C(11)); 127.97 (*d*, C(7)); 132.8 (*s*, C(12)); 133.4 (*s*, C(8)); 134.4 (*s*, C(15)); 139.2 (*d*, C(16)). HR-MS: 338.2001 ($C_{20}H_{31}ClO_2^+$; calc. 338.2014). Anal. calc. for $C_{20}H_{31}ClO_2$: C 70.88, H 9.22; found: C 70.62, H 8.99.

17-Chloro-7,16-secotrinervita-7,11,15-triene-2α,3α-diol Diacetate (=*(1*RS,*12*RS,*13*RS,*14*SR*)-16-(Chloromethyl)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8,15-triene-13,14-diol Diacetate*; **31**). A soln. of **30** (107 mg, 0.32 mmol), pyridine (0.15 ml, 1.86 mmol), Ac_2O (0.14 ml, 1.48 mmol), and *N*,*N*-dimethylpyridin-4-amine (DMAP; 5 mg) in CH_2Cl_2 (5 ml) was stirred at 25° for 5 h. Then MeOH (1 ml) and H_2O (5 ml) were added. The mixture was extracted with AcOEt (2 × 15 ml), the org. phase successively washed with sat. aq. $CuSO_4$ soln. (5 × 3 ml) and then brine (3 × 4 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 4:1): 133 mg (100%) of **31**. Colorless prisms. M.p. 150–152° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.04 (*s*, Me(18)); 1.19 (*tdd*, *J* = 3.5, 12.2, 13.5, H–C(14)); 1.33 (*ddd*, *J* = 2.5, 5.8, 14.2, H–C(5)); 1.47 (*s*, Me(19)); 1.67 (*s*, Me(20)); 1.78 (*ddd*, *J* = 2.5, 12.5, 14.2, H–C(5)); 1.80 (*dddd*, *J* = 1.9, 4.6, 12.9, 13.5, H–C(14)); 1.93–2.16 (*m*, H–C(6), H–C(10), 2 H–C(13)); 2.02 (*s*, Ac); 2.06 (*s*, Ac); 2.25–2.30 (*m*, 2 H–C(9)); 2.34 (*dddd*, *J* = 2.2, 10.7, 12.5, 15.6, H–C(6)); 2.51 (*dddd*, *J* = 8.3, 9.8, 11.3, 14.7, H–C(10)); 2.85 (br. *d*, *J* = 12.2, H–C(1)); 4.04 (*d*, *J* = 11.0, H–C(17)); 4.07 (*d*, *J* = 11.0, H–C(17)); 4.95 (br. *d*, *J* = 11.3, H–C(11)); 5.30 (br. *d*, *J* = 10.7, H–C(7)); 5.42–5.46 (*m*, H–C(2), H–C(16)); 5.74 (*d*, *J* = 3.1, H–C(3)). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.4 (*q*, C(19)); 16.0 (*q*, C(20)); 20.4 (*t*, C(14)); 21.0 (*q*, 2 MeCO); 25.1 (*t*, C(6)); 25.5 (*t*, C(10)); 25.5 (*q*, C(18)); 34.8 (*d*, C(1)); 36.0 (*t*, C(13)); 38.5 (*t*, C(9)); 39.2 (*t*, C(5)); 40.8 (*s*, C(4)); 47.5 (*t*, C(17)); 68.8 (*d*, C(2)); 72.9 (*d*, C(3)); 128.0 (*d*, C(7)); 128.8 (*d*, C(11)); 132.3 (*s*, C(12)); 133.6 (*s*, C(8)); 134.8 (*s*, C(15)); 137.4 (*d*, C(16)); 170.9 (*s*, Me*C*O); 171.1 (*s*, Me*C*O). HR-MS: 422.2222 ($C_{24}H_{35}O_4Cl^+$; calc. 422.2224). Anal. calc. for $C_{24}H_{35}ClO_4$: C 68.15, H 8.34; found: C 67.90, H 8.47.

17-Chloro-2α,3α-bis(methoxymethoxy)-7,16-secotrinervita-7,11,15-triene (=*(1*RS,*12*RS,*15*SR,*16*RS*)-13-(chloromethyl)-15,16-bis(methoxymethoxy)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8,14-triene*; **36**). Under

N_2, a soln. of **20** (55 mg, 0.14 mmol) and PPh_3 (46 mg, 0.18 mmol) in CCl_4 (1 ml) was stirred at 70° for 24 h. After cooling, H_2O (0.5 ml) and sat. aq. $NaHCO_3$ soln. (0.5 ml) were added, and the mixture was extracted with AcOEt (3 × 3 ml). The org. phase was washed with brine (3 × 3 ml), dried (Na_2SO_4), and evaporated and the residue purified by CC (hexane/AcOEt 25:1): 36 mg (63%) of **36**. Colorless prisms. M.p. 95–97° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$): *Tables 1* and *2*. HR-MS: 426.2529 ($C_{24}H_{39}ClO_4^+$; calc. 426.2537). Anal. calc. for $C_{24}H_{39}ClO_4$: C 67.50, H 9.21; found: C 67.30, H 9.25.

17-Chloro-2α,3α-bis(methoxymethoxy)-7,16-secotrinervita-7,11-diene (= *(1*RS*,12*RS*,13*SR*,15*SR*,16*RS*)-13-(Chloromethyl)-15,16-bis(methoxymethoxy)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8-diene*; **37**). As described for **36**, with **21** (335 mg, 0.82 mmol). CC (hexane/AcOEt 23:1) gave 234 mg (67%) of **37**. Colorless prisms. M.p. 93–95° (hexane). IR (CCl_4): 2912, 1444, 1152, 1090, 1026, 916. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.03 (*ddd*, *J* = 3.4, 4.3, 14.7, H–C(5)); 1.05 (*s*, Me(18)); 1.21 (*dd*, *J* = 3.1, 13.0, H–C(16)); 1.24–1.33 (*m*, H–C(1), H–C(14)); 1.50 (*ddd*, *J* = 4.0, 11.0, 12.5, H–C(14)); 1.60 (*s*, Me(19)); 1.62 (*s*, Me(20)); 1.74 (*t*, *J* = 13.0, H–C(16)); 1.91–2.09 (*m*, H–C(5), H–C(6), H–C(10), H–C(13)); 2.13 (*dt*, *J* = 4.0, 12.5, H–C(13)); 2.18 (*ddd*, *J* = 3.4, 12.7, 14.2, H–C(9)); 2.25–2.36 (*m*, H–C(9), H–C(15)); 2.50 (*dddd*, *J* = 3.7, 10.4, 12.7, 14.4, H–C(10)); 2.54 (*dtd*, *J* = 3.4, 11.3, 14.5, H–C(6)); 3.36 (*s*, *Me*OCH$_2$O); 3.49 (*s*, *Me*OCH$_2$O); 3.59 (*d*, *J* = 3.7, 2 H–C(17)); 3.94 (*d*, *J* = 3.7, H–C(2)); 4.03 (*d*, *J* = 3.7, H–C(3)); 4.58 (*d*, *J* = 6.4, MeOC*H*$_2$O); 4.65 (*d*, *J* = 6.7, MeOC*H*$_2$O); 4.71 (br. *d*, *J* = 10.4, H–C(11)); 4.80 (*d*, *J* = 6.4, MeOC*H*$_2$O); 4.84 (*d*, *J* = 6.7, MeOC*H*$_2$O); 5.37 (br. *d*, *J* = 11.3, H–C(7)). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.3 (*q*, C(19)); 16.0 (*q*, C(20)); 20.7 (*t*, C(14)); 24.9 (*q*, C(18)); 25.1 (*t*, C(6)); 25.4 (*t*, C(10)); 31.5 (*d*, C(15)); 36.0 (*t*, C(5)); 36.1 (*t*, C(13)); 38.3 (*s*, C(4)); 39.0 (*d*, C(1)); 39.6 (*t*, C(9)); 39.7 (*t*, C(16)); 49.7 (*t*, C(17)); 55.5 (*q*, *Me*OCH$_2$O); 55.9 (*q*, *Me*OCH$_2$O); 73.1 (*d*, C(2)); 79.3 (*d*, C(3)); 95.5 (*t*, MeO*C*H$_2$O); 97.5 (*t*, MeO*C*H$_2$O); 126.9 (*d*, C(7)); 127.7 (*d*, C(11)); 132.9 (*s*, C(8)); 133.5 (*s*, C(12)). HR-MS: 428.2682 ($C_{24}H_{41}ClO_4^+$; calc. 428.2693). Anal. calc. for $C_{24}H_{41}ClO_4$: C 67.19, H 9.63; found: C 66.94, H 9.70.

2α,3α-Bis(methoxymethoxy)-7,16-secotrinervita-7,11-diene (= *(1*RS*,12*RS*,13*RS*,14*SR*,16*SR*)-13,14-Bis(methoxymethoxy)-1,5,9,16-tetramethylbicyclo[10.2.2]hexadeca-4,8-diene*; **39**). Under N_2, a soln. of **21** (107 mg, 0.26 mmol), TsCl (100 mg, 0.52 mmol), DMAP (25.5 mg, 0.21 mmol), and Et_3N (0.061 ml, 0.44 mmol) in CH_2Cl_2 (5 ml) was stirred at 25° for 17 h. The mixture was diluted with AcOEt (15 ml), the org. phase washed successively with sat. aq. NH_4Cl soln. (3 × 3 ml), sat. aq. $NaHCO_3$ soln. (3 × 3 ml), and brine (3 × 3 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 10:1): 131 mg (89%) of the tosylate of **21**. Colorless prisms (hexane). M.p. 151–153°. IR (CCl_4): 2948, 1452, 1378, 1150, 1096, 1028, 916. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.95 (*td*, *J* = 3.4, 14.2, H–C(5)); 0.98 (*s*, Me(18)); 1.05 (*dd*, *J* = 3.0, 13.1, H–C(16)); 1.18–1.29 (*m*, H–C(1), H–C(14)); 1.35 (*ddd*, *J* = 4.0, 11.0, 12.5, H–C(14)); 1.49 (*s*, Me(19)); 1.51 (*t*, *J* = 13.1, H–C(16)); 1.56 (*s*, Me(20)); 1.87–2.04 (*m*, H–C(5), H–C(6), H–C(10), H–C(13)); 2.07 (*dt*, *J* = 4.0, 12.9, H–C(13)); 2.12–2.20 (*m*, H–C(9), H–C(15)); 2.28 (br. *d*, *J* = 13.8, H–C(9)); 2.41 (*dddd*, *J* = 5.2, 10.1, 12.8, 14.5, H–C(10)); 2.46 (*dddd*, *J* = 3.4, 10.4, 12.0, 13.6, H–C(6)); 2.46 (*s*, *Me*C$_6$H$_4$SO$_3$); 3.33 (*s*, *Me*OCH$_2$O); 3.46 (*s*, *Me*OCH$_2$O); 3.87 (*d*, *J* = 3.4, H–C(2)); 3.93 (*dd*, *J* = 3.7, 14.1, H–C(17)); 3.94 (*d*, *J* = 3.4, H–C(3)); 3.95 (*dd*, *J* = 4.6, 14.1, H–C(17)); 4.54 (*d*, *J* = 6.7, MeOC*H*$_2$O); 4.62 (*d*, *J* = 6.8, MeOC*H*$_2$O); 4.68 (br. *d*, *J* = 10.1, H–C(11)); 4.76 (*d*, *J* = 6.7, MeOC*H*$_2$O); 4.80 (*d*, *J* = 6.8, MeOC*H*$_2$O); 5.30 (br. *d*, *J* = 10.4, H–C(7)); 7.36 (*d*, *J* = 8.0, 2 MeC$_6$*H*$_4$SO$_3$); 7.79 (*d*, *J* = 8.0, 2 MeC$_6$*H*$_4$SO$_3$). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.0 (*q*, C(19)); 15.6 (*q*, C(20)); 20.9 (*t*, C(14)); 21.6 (*q*, *Me*C$_6$H$_4$SO$_3$); 24.6 (*q*, C(18)); 25.1 (*t*, C(6)); 25.3 (*t*, C(10)); 29.9 (*d*, C(15)); 36.0 (*t*, C(5)); 36.1 (*t*, C(13)); 38.2 (*s*, C(4)); 38.7 (*d*, C(1)); 38.7 (*t*, C(16)); 39.5 (*t*, C(9)); 55.5 (*q*, *Me*OCH$_2$O); 55.9 (*q*, *Me*OCH$_2$O); 73.0 (*d*, C(2)); 73.1 (*t*, C(17)); 79.2 (*d*, C(3)); 95.5 (*t*, MeO*C*H$_2$O); 97.5 (*t*, MeO*C*H$_2$O); 126.8 (*d*, C(7)); 127.8 (*d*, C(11)); 128.0 (*d*, 2 MeC$_6$*H*$_4$SO$_3$); 129.8 (*d*, 2 MeC$_6$*H*$_4$SO$_3$); 132.9 (*s*, C(8)); 133.0 (*s*, MeC$_6$*H*$_4$SO$_3$); 133.3 (*s*, C(12)); 144.7 (*s*, MeC$_6$*H*$_4$SO$_3$). HR-MS: 564.3132 ($C_{31}H_{48}O_7S^+$; calc. 564.3121). Anal. calc. for $C_{31}H_{48}O_7S$: C 65.93, H 8.57; found: C 65.83, H 8.86.

$LiAlH_4$ (90 mg, 2.37 mmol) was added to a soln. of the tosylate of **21** (408 mg, 0.72 mmol) in THF (20 ml) at 0°, and the mixture was stirred at 25° for 18 h after the cooling bath was removed. AcOEt (15 ml) was added, the org. phase washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 8:1): 106 mg (37%) of **39** (procedure not optimized). Colorless oil. IR (CCl_4): 2916, 1448, 1370, 1170, 1154, 1026, 914. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.77 (*d*, *J* = 6.4, Me(17)); 0.93 (br. *t*, *J* = 11.3, H–C(1)); 0.98 (*td*, *J* = 4.0, 14.4, H–C(5)); 1.04 (*s*, Me(18)); 1.16 (*dd*, *J* = 3.4, 13.1, H–C(16)); 1.24 (*tdd*, *J* = 4.0, 11.3, 13.8, H–C(14)); 1.27 (*t*, *J* = 13.1, H–C(16)); 1.43 (*dddd*, *J* = 2.2, 5.0, 12.0, 13.8, H–C(14)); 1.55 (*s*, Me(19), Me(20)); 1.86–2.05 (*m*, H–C(6), H–C(10), H–C(13), H–C(15)); 2.95 (*ddd*, *J* = 4.3, 12.5, 14.4, H–C(5)); 2.08 (*ddd*, *J* = 4.3, 12.0, 14.1, H–C(13)); 2.19 (*ddd*, *J* = 3.4, 12.5, 14.2, H–C(9)); 2.31 (br. *d*, *J* = 14.2, H–C(9)); 2.46 (*dddd*, *J* = 4.0, 10.4, 12.5, 14.5, H–C(10)); 2.47 (*dddd*, *J* = 4.0, 11.0, 12.5, 14.3, H–C(6)); 3.36 (*s*, *Me*OCH$_2$O); 3.48 (*s*, *Me*OCH$_2$O); 3.83 (*d*, *J* = 3.4, H–C(2)); 3.93 (*d*, *J* = 3.4, H–C(3)); 4.58 (*d*, *J* = 6.4, MeOC*H*$_2$O); 4.63

(d, $J = 6.7$, MeOCH_2O); 4.73 (br. d, $J = 10.4$, H–C(11)); 4.80 (d, $J = 6.4$, MeOCH_2O); 4.84 (d, $J = 6.7$, MeOCH_2O); 5.37 (br. d, $J = 11.0$, H–C(7)). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.1 (q, C(19)); 15.3 (q, C(20)); 19.7 (q, C(17)); 21.4 (t, C(14)); 24.3 (d, C(15)); 24.9 (q, C(18)); 25.3 (t, C(6)); 25.3 (t, C(10)); 36.3 (t, C(5)); 36.6 (t, C(13)); 38.4 (s, C(4)); 39.7 (t, C(16)); 42.4 (d, C(1)); 45.4 (t, C(9)); 55.4 (q, *Me*OCH$_2$O); 55.9 (q, *Me*OCH$_2$O); 73.6 (d, C(2)); 80.0 (d, C(3)); 95.4 (t, MeOCH_2O); 97.5 (t, MeOCH_2O); 127.2 (d, C(7)); 128.0 (d, C(11)); 132.3 (s, C(8)); 133.4 (s, C(12)). HR-MS: 394.3088 ($C_{24}H_{42}O_4^+$; calc. 394.3083).

17-Chloro-7,16-secotrinervita-7,11-diene-2α,3α-diol (= *(1*RS,*12*RS,*13*RS,*14*SR,*16*SR*)-16-(Chloromethyl)-1,5,9-trimethylbicyclo[10.2.2]hexadeca-4,8-diene-13,14-diol*; **38**). A soln. of **37** (101 mg, 0.24 mmol) in 2M HCl/MeOH (3 ml) was stirred at 25° for 18 h. After addition of H_2O (10 ml), the mixture was extracted with AcOEt (3 × 5 ml). The combined org. phase was washed with sat. aq. $NaHCO_3$ soln. (2 × 3 ml) and then brine (3 × 3 ml), dried (Na_2SO_4), and evaporated and the residue purified by CC (hexane/AcOEt 8:1): 82 mg (98%) of **38**. Colorless needles. M.p. 153–155° (hexane). IR (CCl_4): 3596, 2948, 2912, 1542, 1444, 1108. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.00 (s, Me(18)); 1.08 (td, $J = 4.0$, 14.4, H–C(5)); 1.19 (dd, $J = 4.0$, 12.5, H–C(16)); 1.27 (tt, $J = 4.0$, 13.1, H–C(14)); 1.41 (br. t, $J = 11.5$, H–C(1)); 1.54 (ddd, $J = 4.0$, 11.5, 13.1, H–C(14)); 1.61 (s, Me(19)); 1.62 (s, Me(20)); 1.72 (t, $J = 12.5$, H–C(16)); 1.93 (ddd, $J = 4.3$, 12.5, 14.4, H–C(5)); 1.92–2.15 (m, H–C(6), H–C(10), H–C(13)); 2.12 (dt, $J = 4.0$, 12.7, H–C(13)); 2.16 (ddd, $J = 3.4$, 12.5, 14.2, H–C(9)); 2.30 (qdd, $J = 4.0$, 11.5, 12.5, H–C(15)); 2.30 (br. d, $J = 14.2$, H–C(9)); 2.50 ($dddd$, $J = 3.4$, 10.4, 12.5, 14.4, H–C(10)); 2.54 ($dddd$, $J = 4.0$, 11.0, 12.5, 14.5, H–C(6)); 3.61 (d, $J = 4.0$, 2 H–C(17)); 3.97 (d, $J = 4.0$, H–C(2)); 4.06 (d, $J = 4.0$, H–C(3)); 4.74 (br. d, $J = 10.4$, H–C(11)); 5.20 (br. d, $J = 11.0$, H–C(7)). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.5 (q, C(19)); 15.9 (q, C(20)); 20.5 (t, C(14)); 24.8 (q, C(18)); 25.1 (t, C(6)); 25.2 (t, C(10)); 30.9 (d, C(15)); 35.9 (t, C(5)); 36.7 (t, C(13)); 38.3 (s, C(4)); 38.9 (d, C(1)); 39.5 (t, C(9), C(16)); 49.6 (t, C(17)); 70.4 (d, C(2)); 72.2 (d, C(3)); 126.6 (d, C(7)); 127.9 (d, C(11)); 133.4 (s, C(8), C(12)). HR-MS: 340.2179 ($C_{20}H_{33}ClO_2^+$; calc. 340.2169). Anal. calc. for $C_{20}H_{33}ClO_2$: C 70.46, H 9.76; found: C 70.13, H 10.03.

Trinervita-7,11,15(17)-triene-2α,3α-diol (= *(1*RS,*11*RS,*12a*SR,*13*RS,*14*SR*)-1,2,3,5,6,9,10,11,12,12a-Decahydro-1,4,8-trimethyl-12-methylidene-1,11-ethanocyclopentacycloundecene-13,14-diol*; **32**). Under N_2, a soln. of **30** (101 mg, 0.30 mmol) in THF (4 ml) was added dropwise to a stirred soln. of $AgClO_4$ (93 mg, 0.45 mmol) in THF (15 ml) at −20°. After stirring at −20° for 20 h, the mixture was poured into brine (5 ml) and extracted with Et_2O (3 × 20 ml). The combined org. extract was washed with brine (2 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 4:1): 75 mg (83%) of a white solid. The solid was purified by HPLC (*ERC SILICA 2744* column (30 × 300 mm), hexane/AcOEt 4:1, flow 18 ml/min, RI detector): 61 mg (68%) of **32** and 5 mg (5%) of *trinervita-8 (19),11,15(17)-triene-2α,3α-diol* (= *(1*RS,*3a*RS,*11*RS,*12a*SR,*13*SR,*14*SR*)-1,2,3,3a,4,5,6,9,10,11,12,12a-Dodecahydro-1,8-dimethyl-4,12-dimethylidene-1,11-ethanocyclopentacycloundecene-13,14-diol*; **33**).

Data of **32**: Colorless prisms. M.p. 148–150° (hexane). IR (CCl_4): 3580, 2932, 1448, 1396, 1084. ^{1}H-NMR and ^{13}C-NMR: *Tables 1* and *2*. HR-MS: 302.2238 ($C_{20}H_{30}O_2^+$; calc. 302.2247). Anal. calc. for $C_{20}H_{30}O_2$: C 79.42, H 10.00; found: C 79.02, H 9.62.

Data of **33**: Colorless prisms. M.p. 142–144° (hexane). IR (KBr): 3404, 2908, 1446, 1310, 1116, 1034. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.00 (s, Me(18)); 1.12 (dt, $J = 7.5$, 12.5, H–C(5)); 1.26 (d, $J = 7.5$, OH–C(2)); 1.52 ($dddd$, $J = 3.5$, 7.0, 11.0, 14.5, H–C(14)); 1.53 (s, Me(20)); 1.73 (td, $J = 7.5$, 14.0, H–C(6)); 1.76–1.86 (m, H–C(9)); 1.91 ($dddd$, $J = 3.5$, 7.0, 10.5, 14.5, H–C(14)); 1.96–2.06 (m, H–C(6), H–C(10), H–C(13)); 2.07 (dd, $J = 7.0$, 12.5, H–C(5)); 2.21 (d, $J = 9.0$, OH–C(3)); 2.28 (dt, $J = 7.0$, 11.0, H–C(13)); 2.31–2.50 (m, H–C(1), H–C(9), H–C(10)); 2.62 (d, $J = 12.5$, H–C(16)); 2.83 (td, $J = 7.5$, 12.5, H–C(7)); 3.47 (dd, $J = 3.5$, 9.0, H–C(3)); 3.67 (ddd, $J = 3.0$, 3.5, 7.5, H–C(2)); 4.91 (s, H–C(17)); 5.07 (s, H–C(19)); 5.10 (s, H–C(19)); 5.11 (s, H–C(17)); 5.04–5.17 (m, H–C(11)). ^{13}C-NMR (125 MHz, $CDCl_3$): 15.5 (q, C(20)); 22.1 (q, C(18)); 25.2 (t, C(10)); 25.9 (t, C(14)); 28.9 (t, C(6)); 35.9 (t, C(9)); 37.8 (t, C(13)); 38.1 (t, C(5)); 41.4 (d, C(1)); 49.4 (d, C(7)); 50.2 (s, C(4)); 59.7 (d, C(16)); 72.3 (d, C(3)); 77.9 (d, C(2)); 109.6 (t, C(19)); 115.0 (t, C(17)); 129.5 (d, C(11)); 130.6 (s, C(12)); 145.6 (s, C(15)); 150.2 (s, C(8)). HR-MS: 302.2259 ($C_{20}H_{30}O_2^+$; calc. 302.2247). Anal. calc. for $C_{20}H_{30}O_2$: C 79.42, H 10.00; found: C 79.16, H 9.82.

Trinervita-7,11,15(17)-triene-2α,3α-diol Diacetate (= *(1*RS,*11*RS,*12a*SR,*13*SR,*14*SR*)-1,2,3,5,6,9,10,11,12,12a-Decahydro-1,4,8-trimethyl-12-methylidene-1,11-ethanocyclopentacycloundecene-13,14-diol Diacetate*; **32** (OAc instead of OH)). A soln. of **31** (122 mg, 0.29 mmol) and $AgClO_4$ (91 mg, 0.43 mmol) in anh. THF (15 ml) was stirred at 25° for 6 h under N_2. Then brine (10 ml) was added, the mixture extracted with Et_2O (20 ml, 3 times), the combined org. extract washed with brine (5 ml, twice), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 6:1): 106 mg (95%) **32**/**33** (both OAc instead of OH) 6:1. A soln. of this 6:1 mixture (12 mg) in 2M KOH/MeOH (1 ml) was stirred at 25° for 15 h, and H_2O (2 ml) was added. The mixture

was extracted with Et_2O (3×10 ml), washed with brine, dried (Na_2SO_4), and evaporated: 10 mg (100%) of **32**/**33** 6:1. For data, see above.

Data of **32** (OAc instead of OH): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.08 (*s*, Me(18)); 1.05–1.14 (*m*, H–C(5)); 1.22–1.31 (*m*, H–C(14)); 1.54 (*s*, Me(20)); 1.62 (*s*, Me(19)); 1.55–1.70 (*m*, H–C(5), H–C(9)); 1.81–1.88 (*m*, H–C(13), H–C(14)); 2.01 (*s*, 2 Ac); 1.98–2.09 (*m*, H–C(10), H–C(13)); 2.15 (*tt*, $J = 4.0, 12.0$, H–C(10)); 2.27 (br. *d*, $J = 4.9$, H–C(1)); 2.36 (*dd*, $J = 7.6, 16.8$, H–C(6)); 2.44–2.57 (*m*, H–C(6)); 2.65 (*dt*, $J = 4.0, 12.7$, H–C(9)); 2.99 (*s*, H–C(16)); 4.90 (*s*, H–C(17)); 4.92 (*d*, $J = 3.2$, H–C(3)); 5.00 (*s*, H–C(17)); 4.97–5.03 (*dd*, $J = 4.3, 12.0$, H–C(11)); 5.24 (*dd*, $J = 2.0, 3.2$, H–C(2)). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.6 (*q*, C(20)); 18.8 (*q*, C(19)); 20.7 (*q*, *Me*CO); 20.8 (*q*, C(18)); 20.9 (*q*, *Me*CO); 24.2 (*t*, C(10)); 24.7 (*t*, C(14)); 30.4 (*t*, C(6)); 32.6 (*t*, C(9)); 36.1 (*t*, C(5)); 39.6 (*t*, C(13)); 40.9 (*d*, C(1)); 49.2 (*s*, C(4)); 61.4 (*d*, C(16)); 72.2 (*d*, C(3)); 75.8 (*d*, C(2)); 113.0 (*t*, C(17)); 125.6 (*d*, C(11)); 129.9 (*s*, C(8)); 132.6 (*s*, C(12)); 135.2 (*s*, C(7)); 146.1 (*s*, C(15)); 170.7 (*s*, Me*C*O); 170.9 (*s*, Me*C*O).

Kempa-7,11-diene-2α,3α-diol (= *(2a*RS,*3*SR,*4*RS,*4aRS,10b*RS,*10c*SR*)-1,2,2a,3,4,4a,5,6,8,9,10b,10c-Dodecahydro-2a,7,10,10c-tetramethylnaphth[2,1,8*-cde*]azulene-3,4-diol* **35** *from* **30**. A soln. of **30** (60 mg, 0.18 mmol) and $AgClO_4$ (55 mg, 0.27 mmol) in anh. THF (2 ml) was stirred at 20° for 2 h. Then brine (2 ml) was poured into the mixture, the mixture extracted with Et_2O (3×10 ml), the combined org. extract washed with brine (2×3 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 4:1): 27 mg (50%) of **35**. M.p. 128–130° (hexane). ^{1}H-NMR and ^{13}C-NMR: *Tables 1* and *2*. HR-MS: 302.2254 ($C_{20}H_{30}O_2^+$; calc. 302.2247). Anal. calc. for $C_{20}H_{30}O_2$: C 79.42, H 10.00; found: C 79.15, H 10.48.

Kempa-7,11-diene-2α,3α-diol (**35**) *from* **32**. ^{t}BuCl (0.042 ml, 0.38 mmol) and then $AgClO_4$ (20 mg, 0.097 mmol) were successively added to a soln. of **32** (22 mg, 0.073 mmol) in anh. THF (2 ml) at 25°. The mixture was stirred for 30 min. Then brine (1 ml) and H_2O (1 ml) were added. The mixture was extracted with Et_2O (3×10 ml), the extract washed with brine (2×5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 4:1): 19 mg (86%) of **35**.

Kempa-7,11-diene-2α,3α-diol (**35**) *from* **23**: As described for **35** from **32**, with **23** (790 mg, 2.47 mmol): 365 mg (49%) of **35** after CC and then recrystallization from hexane.

X-Ray Crystal Structure of **36**. X-Ray crystal data for $C_{24}H_{39}ClO_4$ (M_r 427.02): monoclinic space group $P2_1/n$, $D_c = 1.157$ g cm^{-3}, $Z = 4$, $a = 10.080(1)$, $b = 22.998(2)$, $c = 10.793(1)$ Å, $\beta = 101.48(1)°$, $V = 2451.9(5)$ Å^3, MoK_a radiation, $l = 0.71069$ Å, $2.53 \leq q \leq 27.50°$, 5616 unique reflections, T 296 K. The structure was solved by direct methods and refined by full-matrix least-squares analysis [13][14]. All non-H-atoms were refined anisotropically, H-atoms isotropically. All-data refinement of 419 parameters based on F^2 converged at $R(F) = 0.0613$ and $wR(F^2) = 0.1787$. Crystallographic data (excluding $F_o - F_c$ listings) for compound **36** have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-147341. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

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