Synthesis of (±)-Trinervitadiene-2,3-diol[1)][2)]

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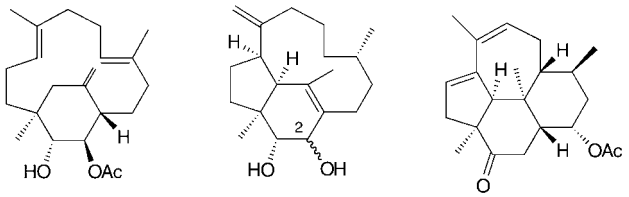
The first synthesis of trinervita-1(15),8(19)-dien-2β,3α-diol (**2a**) and its 2α-isomer **2b**, which have been isolated from termite soldiers, where they are used as defense chemicals, is documented starting from geranylgeranioic acid in 33 steps. The route for construction of the key intermediate of the trinervitane skeleton **8** has been developed previously (*Scheme 1*). Noteworthy features include the efficient construction of the trinervitane framework from the corresponding bicyclic 7(16)-secotrinervitane skeleton and Me_3SiCl (TMSCl)-induced ring-opening of tetrasubstituted epoxide to give the corresponding allyl alcohols (*Scheme 7*). The synthetic route developed in the present study seems applicable to the syntheses of other trinervitane-type natural products.

Introduction. – The trinervitanes are constituents of the secretion of soldiers of the termite species *Trinervitermes gratiosus* that include biogenetically related cyclic diterpenes [3] such as bicyclic 7,16-secotrinervitatriene-2,3-diol 2-acetate **1** [4], tricyclic trinervitadiene-2β,3α-diol **2a** [5], and tetracyclic 14-acetoxykempa-6,8-dien-3-one **3** [1][6]. A quarter-century ago, *Prestwich et al.* reported the first isolation and structure determination of **2a** [5]; later, **2a** and the 2α-isomer **2b** were also described by *Vrkoc et al.* [7]. The trinervitanes are reported [8] to be among the defense substances produced by termites.



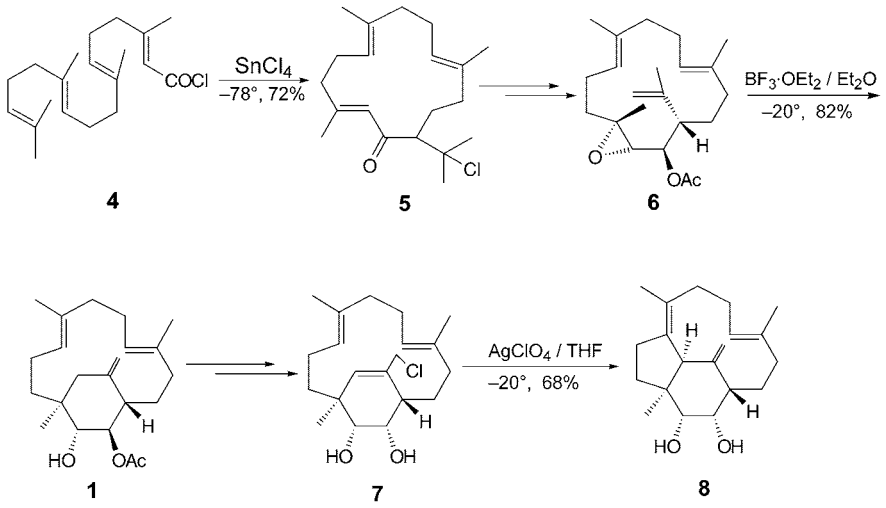
1 **2a** 2β-OH **2b** 2α-OH **3**

In spite of the early discovery and unique skeleton, the total synthesis of trinervitane-type natural products has not been reported. We have been very interested in the synthesis of these biologically and skeletally attractive diterpenoids. The synthetic strategy associated with our exploration of these natural products has been based on biogenetic consideration [9], and we have exploited and accumulated the construction routes of a key intermediate that possesses the trinervitane skeleton,

1) Part 64 of the series of cyclization of polyenes. Part 63: [1]
2) Partially published in a preliminary communication [2].

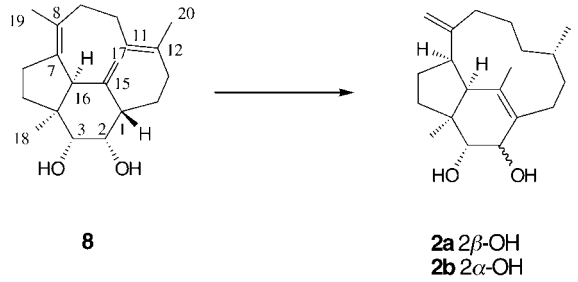
starting from geranylgeranioic acid chloride **4**, as described in a previous paper (*Scheme 1*) [10]. After efficient construction of the cembrene skeleton **5**, the second cyclization from epoxy acetate **6**, easily derived from **5**, was achieved to form the natural product, 7,16-secotrinervitatriene-2,3-diol 2-acetate **1**. The allyl chloride **7**, derived from **1** by the sequential reactions, proved to be a suitable intermediate for the stereoselective third cyclization to build the trinervitane skeleton **8**.

Scheme 1. *Construction of Trinervitane Skeleton* **8**



Further study has focused on the conversion of **8** to biologically intriguing trinervitane-type natural products. This paper describes the details of the synthesis of (±)-trinervitadiene-2,3-diols, **2a** and **2b**, from the intermediate **8** [2] (*Scheme 2*).

Scheme 2. *Conversion of the Intermediate* **8** *to the Natural Products* **2a** *and* **2b**

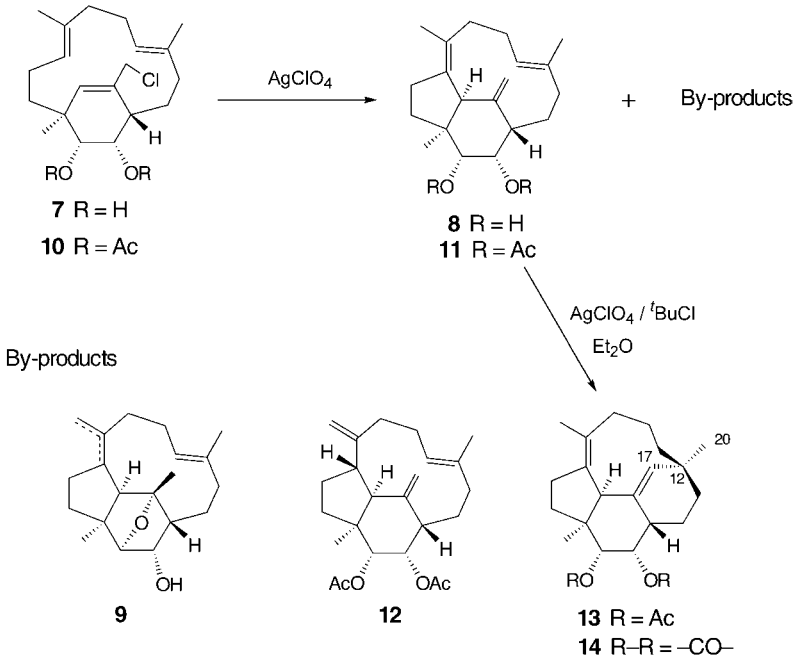


Results and Discussion. – The synthesis of the natural products **2a** and **2b** from the trinervitane intermediate **8** (*Scheme 2*) demands the conversion of three double bonds so as to effect the selective reduction of the trisubstituted C(11)=C(12) bond to the dihydro moiety containing the 12α-Me group, transformation of the exocyclic C(15)=C(17) bond to the tetrasubstituted C(1)=C(15) bond, and the tetrasubstituted

C(7)=C(8) bond to the exocyclic C(8)=C(19) bond. Our tentative oxidation experiment with 3-chloroperbenzoic acid (*m*-CPBA) has revealed that the reactivities of the three C=C bonds in **8** are different enough to carry out the selective transformation of these C=C bonds, the C(11)=C(12) bond being the most reactive one. The existence of a 2-OH group is expected to assist the differentiation of the remaining two C=C bonds.

At the outset of the present study, we aimed to improve the yield of the trinervitane intermediate **8** from the allyl chloride **7** (*Scheme 3*). As reported previously [10], the ring construction of dihydroxy allyl chloride **7** was carried out by means of $AgClO_4$ in THF, affording the trinervitane skeleton **8** in 68% yield along with several kinds of by-products, including the epoxy derivative **9**. To avoid formation of **9**, the cyclization of diacetate **10** was examined under the same conditions, giving a 6:1 mixture of compound **11** and the 8(19)-isomer **12**, which has the 7β-configuration. When the reaction of **10** was carried out in Et_2O instead of THF, formation of the tetracyclic compound **13** was observed as the major by-product. The structure of the by-product **13** was confirmed by NMR spectroscopy of the corresponding carbonate **14**, easily prepared from **13** by saponification with KOH/MeOH, followed by carbonation with 1,1′-carbonyldiimidazole (CDI) in high overall yield. The sequence of C(20)–C(12)–C(17) is evident from HMBC analysis, in which a signal at 38.2 ppm (*s*, C(12)) is clearly correlated with the H-atoms at 1.03 ppm (*s*, Me(20)) and 5.67 ppm (*s*, H–C(17)). The configuration at C(12) was deduced from the mechanism of its

Scheme 3. *Cyclization of 17-Chloro-7,16-secotrinervitanes* **7** *and* **10**



formation and supported by the observation of a clear NOE between H–C(17) and H–C(9) in the ^{1}H-NMR spectrum of **14**.

The formation of **13** may be due to the acid ($HClO_4$)-promoted cyclization of **11**. In fact, treatment of **11** with $HClO_4$, prepared *in situ* from $AgClO_4$ and *t*-BuCl in Et_2O, gave the by-product **13**. The transformation of **10** exclusively to the product **11** was finally achieved by treatment with $AgClO_4$ in ether in the presence of 1 mol-equiv. of pyridine, affording **11** in 93% yield.

The next step was focused on the regio- and face-selective hydrogenation of the diol **8** possessing three different types of C=C bonds. The PtO_2-catalyzed hydrogenation in MeOH afforded a 7:3 mixture of 11,12-dihydro derivatives, revealing that the two remaining C=C bonds at the 7(8) and 15(17) positions are inert under the conditions employed. The separation of the reduction products turned out to be quite problematic since it formed prism-shaped mixed crystals (m.p. 92–94°), and HPLC analysis showed a single peak under several conditions[3]). As regards the reasonable conformation of the macro ring of the diol **8**, two gross structures are possible as shown in *Scheme 4*. The plane of the C(11)=C(12) bond is perpendicular to the cyclohexane ring in one conformation (perpendicular conformation; **PC**) and horizontal in the other conformation (horizontal conformation; **HC**).

The hydrogenation may occur from the opposite faces depending on the conformation, *i.e.*, the perpendicular conformation gives the 12β-Me product by selective H_2 addition from the α-side. The horizontal conformation leads to the 12α-Me isomer by the preferential β-face attack, the opposite α-face being partly masked by the C(15)=C(17) bond. The existence of **8** as the horizontal conformation was deduced by the fact that **8** is easily convertible to the cyclized product **16** under protic conditions ($AgClO_4$ + *t*-BuCl) [10]. The preferred existence of **HC** may be sterically induced, as the sequence from C(11) to C(15) connected with C(1) exists as a chair-like conformation, whereas **PC** shows a sterically unfavorable boat-like conformation. These considerations lead to the conclusion that the major dihydro product possesses 12α-Me configuration derived from the preferential hydrogenation from the β-face of the horizontal conformation.

Expecting a conformational change of the cyclohexane ring of **8**, a five-membered ring was introduced at C(2) and C(3) to give **17**. The incorporation of the cyclic carbonate is expected to restrict significantly the conformational freedom, inducing rigidity to the original conformation of **8**, thereby promoting the horizontal conformation (*i.e.*, **HC**). In fact, a 0.2-ppm upfield shift of H–C(11) of **17** was observed, indicating the change of the chair-type cyclohexane ring of **8** to the twisted form, in which the C(15)=C(17) bond-located more closely to the plane of the C(11)=C(12) bond. The hydrogenation of **17** in CH_2Cl_2 provided a 6:1 mixture of C(12) stereoisomers. It was lucky enough to find that a stereoisomeric mixture of the carbonates **18a** and **18b** was easily separable by flash chromatography. The major carbonate **18a** furnished the 12α-compound **15a**, and **18b** the minor isomer **15b** by alkaline hydrolysis.

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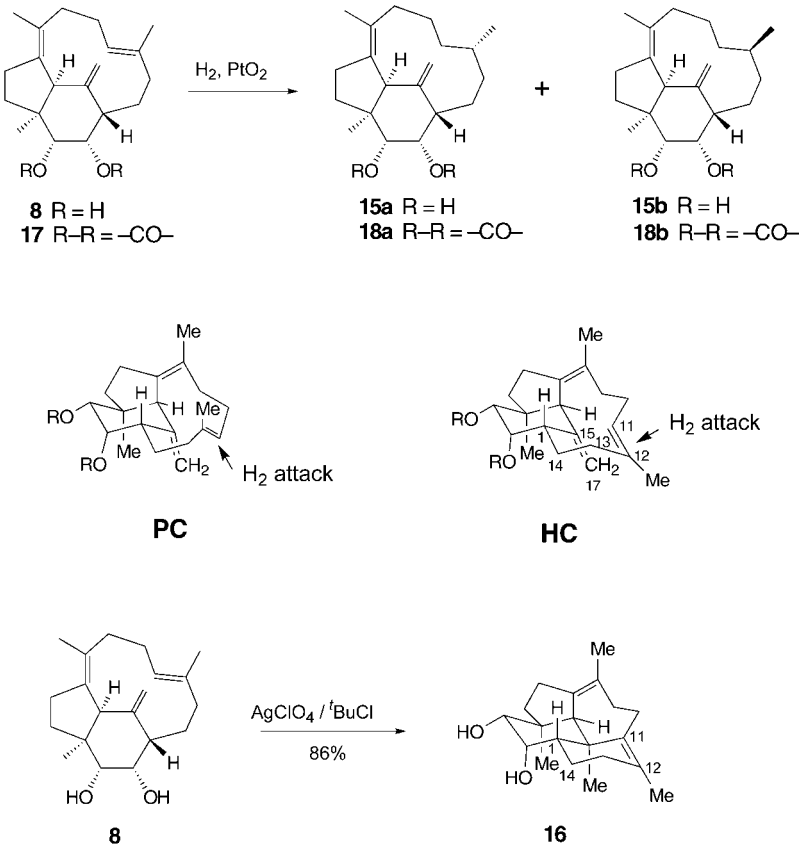
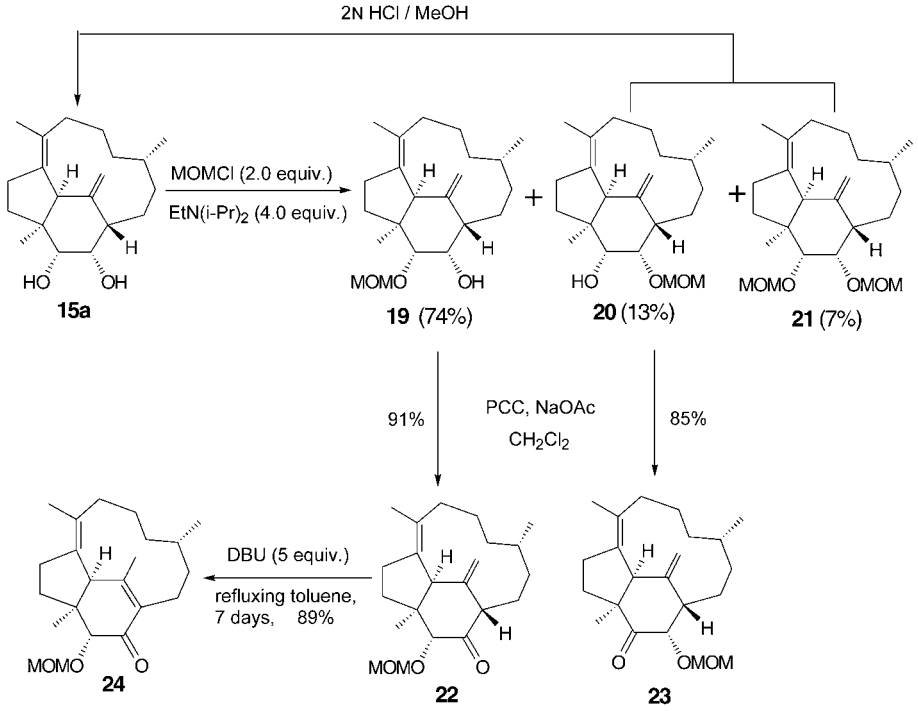
[3]) The X-ray crystallographic analysis of the single crystals displayed the presence of two compounds, **15a** and **15b**, in the crystals.

Scheme 4. *Conformation and Hydrogenation Products of* **8** *and its Carbonate* **17**



Shift of the C(15)=C(17) bond to the 1(15) position of **15a** is expected to be promoted from the corresponding 2-oxo derivative. Prior to the oxidation of the 2-OH group, the selective protection of the OH group at C(3) was carried out as follows. The reaction of **15a** with MOMCl (MOM = methoxymethyl) in the presence of $EtN(i\text{-}Pr)_2$ led to formation of the corresponding 3-MOM ether **19** in 74% yield, accompanied with small amounts of the isomeric 2-MOM ether **20** and bis-MOM ether **21**. After separation of **19**, the remaining MOM ethers, **20** and **21**, were reconverted to the starting material **15a** by acid hydrolysis for the recycling. The position of the MOM group of **19** and **20** was confirmed by the ^{1}H-NMR spectra of the corresponding oxo-derivatives **22** and **23** (*Scheme 5*). The H-atom at C(3) of **22** appeared at 4.07 ppm as a *singlet*, and H–C(2) of **23** showed a *doublet* ($J = 3.6$ Hz) at 3.78 ppm. Treatment of **22** with such bases as NaH, *t*-BuOK, or LDA resulted in recovery of the starting material or complete decomposition of the product, and no isomerized compound was obtained. Effective isomerization was finally found to take place by the action of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 5 equiv.) in refluxing toluene for a week to

Scheme 5. *Preparation of 3-MOM Enone* **24**



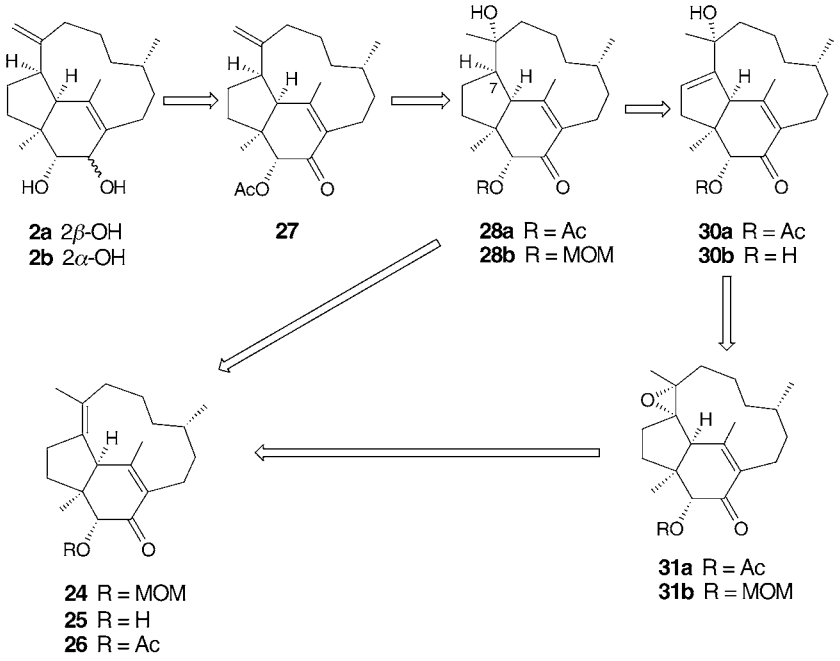
afford **24** in 89% yield. Elevation of the reaction temperature by replacing toluene with refluxing xylene did not have any effect on the outcome of the reaction.

Scheme 6 outlines the planned conversion routes to natural products **2a** and **2b** from the enone **24**. The most facile access to the immediate precursor **27** is, obviously, the hydroboration reaction of **24** and its synthetic equivalents **25** and **26**[4]). The Me group at the 4α-position of **24** was considered to control to some extent the position of hydride addition on the C(7)=C(8) bond, providing predominantly 8-hydroxy enone **28**. It was quite discouraging to note that 7-OH compound **29** was formed exclusively as a diastereoisomeric mixture when **24** was subjected to the hydroboration reaction under standard conditions, followed by oxidative workup (*Scheme 7*). Although the selective formation of **29** cannot be exactly explained, the experimental fact compelled us to detour the preparation of **28** through the allyl alcohol **30**, which might be obtained from the epoxy compound **31**.

The enones **24** and **26** afforded the corresponding α-epoxy derivatives **31b** and **31a** in high yields by *m*-CPBA oxidation. Trials of base-promoted ring opening of **31b** with LDA, LiHMDS, or NaHMDS were all unsuccessful; acid-promoted ring opening of **31a** under controlled conditions led to unfruitful results. On the basis of these unsuccessful results, presumably due to the unstable nature of the allyl alcohol **30** even

[4]) For the preparation, see the *Exper. Part*.

Scheme 6. *Conversion Routes to Natural Products* **2a** *and* **2b** *from the Intermediate* **24**



if it were formed, we explored an alternative less acidic *Lewis* acid, but one with enough acidity to cleave the epoxy ring. We were quite delighted to disclose the unreported reactivity of TMSCl to the hindered tetrasubstituted epoxide. Treatment of **31a** with TMSCl at $-10°$ supplied the allyl alcohol **30a** in 41% yield after purification by column chromatography. The ^{1}H-NMR spectrum of the crude reaction mixture indicated that the reaction proceeded almost quantitatively to give a *ca.* 1:1 mixture of **30a** and its isomer **32**, the latter decomposing more readily during the silica-gel column chromatography. The catalytic hydrogenation of **30a** went smoothly without any problem from the convex face, as in the cases of oxidation with *m*-CPBA, affording **28a** as a single product. The structure of the product was supported by the new *doublet* ($J(7,16) = 11.4$) at δ 2.61 ppm of H–C(16), which had appeared as a *singlet* in the ^{1}H-NMR spectra of the precursors **30a** and **31a**. Dehydration of **28a** with $SOCl_2$ gave a mixture of **26**, **27**, and **33**, which was isolated in 97% yield in a 5:3:1 ratio. Application of the *Burgess* reagent [11] showed no improvement of the yield of **27**. The mixture was separated by $AgNO_3/SiO_2$ column chromatography. Reduction of **27** with $LiAlH_4$ gave **2a** and **2b** in 56 and 44% yields, respectively. The ^{1}H-NMR spectra of natural products **2a** and **2b** [4], and our synthetic compounds are displayed in the *Table*, clearly showing the agreement of each pair within experimental deviation.

In conclusion, we have completed the first total synthesis of trinervita-1(15),8(19)-dien-2β,3α-diol and the 2α-isomer, characterized from termite soldiers a quarter-century ago, in 33 steps starting from geranylgeranioic acid. Noteworthy features include the efficient construction of the trinervitane framework from the corresponding

Scheme 7. *Reactions of* **24** *and* **26** *Directed to the Synthesis of Natural Products*

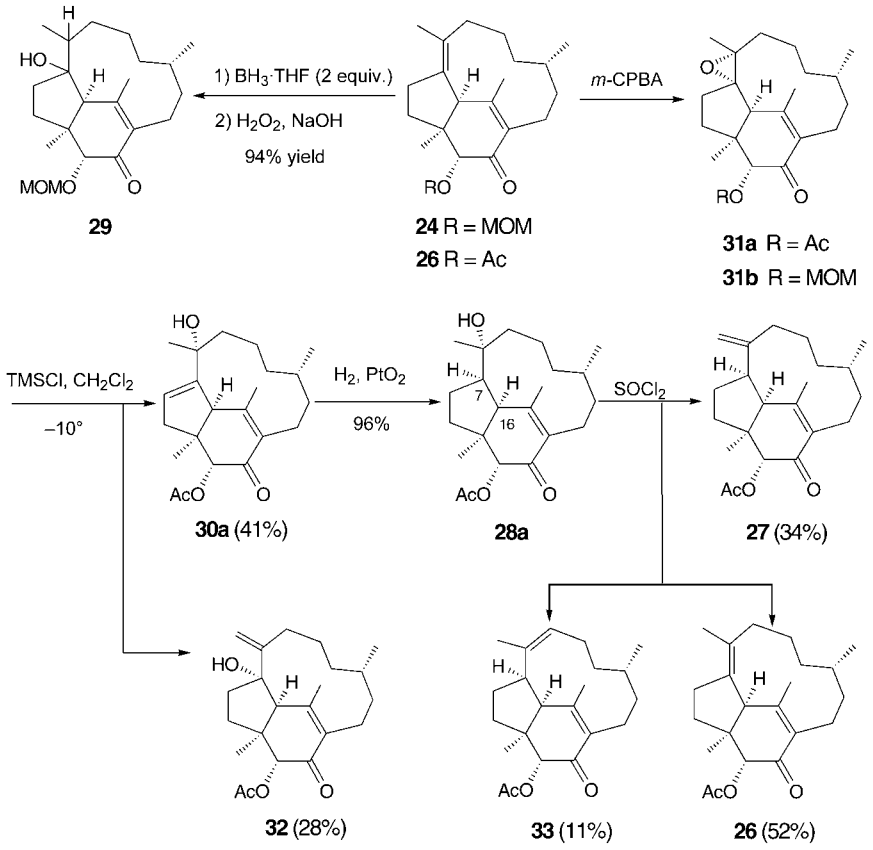


Table 1. *^{1}H-NMR Data of Natural and Synthetic Trinervit-1(15)-ene-2,3-diols* **2a** *and* **2b**

	2a		**2b**	
	Natural (100 MHz)	Synthetic (500 MHz)	Natural (100 MHz)	Synthetic (500 MHz)
H–C(2)	3.96 (*dq*, *J* = 8.9, 1.8)	3.96 (br. *d*, *J* = 8.9)	4.08 (br. *d*, *J* = 5.0, 0.5)	4.07 (*dd*, *J* = 5.2, 5.8)
H–C(3)	3.81 (*d*, *J* = 8.9)	3.83 (*d*, *J* = 8.9)	3.91 (*d*, *J* = 5.0)	3.91[a]) (*dd*, *J* = 5.2, 9.0)
H–C(7)	3.16 (*dt*, *J* = 13, 9.9)	3.16 (*dt*, *J* = 7.9, 11.6)	3.25 (*dt*, *J* = 11.5, 9.5)	3.24 (*dt*, *J* = 12.2, 9.3)
H–C(16)	2.39 (br. *d*, *J* = 12.5)	2.39 (*d*, *J* = 11.6)	2.53 (br. *s*, *J* = 0.5)	2.53 (*d*, *J* = 12.2)
Me(17)	1.74 (*d*, *J* = 1.8)	1.74 (*d*, *J* = 1.9)	1.78 (br. *s*, *J* = 0.5)	1.78 (*s*)
Me(18)	0.99 (*s*)	1.00 (*s*)	1.10 (*s*)	1.10 (*s*)
CH_2(19)	4.77 (*m*); 4.92 (*m*)	4.77 (*m*); 4.93 (*m*)	4.82 (*m*); 4.94 (*m*)	4.83 (*m*); 4.94 (*m*)
Me(20)	0.92 (*d*, *J* = 6.5)	0.92 (*d*, *J* = 6.7)	0.9 (*d*, *J* = 6)	0.89 (*d*, *J* = 6.7)

[a]) *dd* of H–C(3) of synthetic **2b** is due to *J*(2,3) and *J*(3,OH), respectively.

bicyclic 7,16-secotrinervitane skeleton and TMSCl-induced ring opening of a tetrasubstituted epoxide to give the corresponding allyl alcohols. The synthetic route developed in the present study seems applicable to the synthesis of other trinervitane-type natural products, such as the 2-deoxy analogue, trinervita-1(15),8(19)-dien-3α-ol, the position of the OH group being controversial [12].

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. THF and Et_2O were distilled from sodium-benzophenone ketyl, hexane was distilled from P_2O_5 for the respective reaction solvents. Distilled Et_2O and AcOEt were used for extraction. TLC: aluminium sheets coated with silica gel *60 F254*, elution with AcOEt/hexane mixtures; spots were visualized with UV light and then stained with 0.5% anisaldehyde in 2M aq. H_2SO_4. CC (column chromatography): silica gel *60* (Art. 7734, 70–230 mesh); M.p.: *Yanaco MP* apparatus; uncorrected. IR Spectra: films on NaCl windows; *Hitachi 270-30* spectrophotometer. ^{1}H- and ^{13}C-NMR spectra: $CDCl_3$ solns. with Me_4Si as an internal standard, *JEOL* spectrometers; δ in ppm, *J* in Hz. MS: *Hitachi M-80B* spectrometer. Combustion analyses: *Yanaco MT-6 CHN Corder.*

Trinervita-7,11,15(17)-triene-2α,3α-diol Diacetate (**11**). Under N_2, a soln. of **10** (185 mg, 0.44 mmol) in Et_2O (5 ml) was added dropwise to a stirred soln. of $AgClO_4$ (110 mg, 0.53 mmol) and pyridine (53 ml, 0.66 mmol) in Et_2O (2 ml) at 25°. After stirring at 25° for 17 h, the mixture was diluted with Et_2O (10 ml), and washed with brine (2 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue was purified by CC (hexane/AcOEt 20:1): 157 mg (93%) of **11**. Colorless needles. M.p. 139–140° (hexane). ^{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, CDCl3): 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, 170.9 (2 *s*, 2 Me*CO*). Anal. calc. for $C_{24}H_{34}O_4$: C 74.58, H 8.87; found: C 74.29, H 8.90.

*(1*RS*,9*RS*,12*RS*,13*RS*,14*SR*,15*SR*)-1,5,9-Trimethyltetracyclo[7.5.3.0^{4,15}.0^{12,16}]heptadeca-4,16-diene-13,14-diol Diacetate* (**13**). *From the Chloro Derivative* **10**. Under N_2, a soln. of **10** (200 mg, 0.47 mmol) in Et_2O (6 ml) was added dropwise to a stirred soln. of $AgClO_4$ (118 mg, 0.57 mmol) in Et_2O (5 ml) at 25°. After stirring at 25° for 3 h, the mixture was poured into brine (3 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 was purified by CC (hexane/AcOEt 20:1): 177 mg (97%) of **11/13** 1:1.

From the Acetate **11**. Under N_2, a soln. of **11** (20 mg, 0.047 mmol) in Et_2O (5 ml) was added dropwise to a stirred mixture of $AgClO_4$ (13 mg, 0.057 mmol) and *t*-BuCl (7.7 µl, 0.08 mmol) in Et_2O (1 ml) at 25°. After stirring at 25° for 17 h, the mixture was poured into brine (3 ml) and extracted with Et_2O (3 × 10 ml). The combined org. extract was washed with brine (2 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue was purified by CC (hexane/AcOEt 20:1): 19 mg of **11/13** 1:5.

*(1*RS*,9*RS*,12*RS*,13*RS*,14*SR*,15*SR*)-1,5,9-Trimethyltetracyclo[7.5.3.0^{4,15}.0^{12,16}]heptadeca-4,16-diene-13,14-diol Carbonate* (**14**). A soln. of **11/13** 1:1 (118 mg, 0.31 mmol) in 2M KOH/MeOH (5 ml) was stirred at 20° for 4 h. After the addition of H_2O (10 ml), the mixture was extracted with Et_2O (3 × 20 ml), and the combined org. extract was washed with brine (2 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue was purified by CC (hexane/AcOEt 8:1): 82 mg (89%) of **8/13** (R = H) 1:1. After the 1:1 mixture **8/13** (R = H) (82 mg, 0.27 mmol) and 1,1′-carbonyldiimidazole (132 mg, 0.81 mmol) in benzene (3 ml) had been stirred at 20° for 3 h, H_2O (5 ml) and Et_2O (15 ml) were added. The org. phase was dried (Na_2SO_4) and evaporated and the residue was purified by CC (hexane/$CHCl_3$ 3:2): 39 mg (43%) of **14** and 41 mg (46%) of **17**.

Data of **13** *(R = H).* Colorless prisms. M.p. 153–154° (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.90–1.00 (*m*, H–C(10)); 1.08 (*s*, Me(20)); 1.14 (*dt*, *J* = 8.3, 12.5, H–C(5)); 1.18 (*s*, Me(18)); 1.33–1.52 (*m*, 2 H–C(11), 2 H–C(13)); 1.54–1.61 (*m*, 2 H–C(14)); 1.57 (*s*, Me(19)); 1.64–1.76 (*m*, H–C(9), H–C(10)); 2.01 (*dd*, *J* = 6.6,

12.5 Hz, H–C(5)); 2.13 (br. *t*, *J* = 7.6, H–C(1)); 2.21–2.36 (*m*, 2 H–C(6)); 2.48 (*dt*, *J* = 6.4, 12.2, H–C(9)); 3.19 (*s*, H–C(16)); 3.49 (br. *s*, H–C(3)); 3.84 (br. *t*, *J* = 2.7, H–C(2)); 5.56 (*s*, H–C(17)). ^{13}C-NMR (100 MHz, CDCl3): 22.6 (*q*, C(18)); 22.7 (*q*, C(19)); 23.4 (*t*, C(14)); 24.2 (*t*, C(10)); 28.7 (*q*, C(20)); 30.0 (*t*, C(6)); 32.0 (*t*, C(13)); 34.0 (*t*, C(9)); 37.8 (*t*, C(5)); 39.3 (*s*, C(12)); 39.3 (*d*, C(1)); 45.6 (*t*, C(11)); 46.5 (*s*, C(4)); 59.2 (*d*, C(16)); 72.7 (*d*, C(3)); 74.7 (*d*, C(2)); 132.2 (*s*, C(8)); 136.2 (*s*, C(7)); 137.1 (*s*, C(15)); 139.6 (*d*, C(17)). HR-MS: 302.2255 ($C_{20}H_{30}O_2^+$; calc. 302.2246).

Data of **14**. Colorless prisms. M.p. 170–171° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.00 (*m*, H–C(10)); 1.03 (*s*, Me(20)); 1.25 (*s*, Me(18)); 1.40–1.50 (*m*, 2 H–C(5), 2 H–C(13)); 1.50–1.55 (*m*, 2 H–C(11)); 1.62 (*s*, Me(19)); 1.70 (*dt*, *J* = 4.3, 12.2, H–C(9)); 1.70–1.80 (*m*, H–C(10), 2 H–C(14)); 2.30 (*m*, H–C(6)); 2.34 (*ddd*, *J* = 1.7, 5.2, 12.9, H–C(1)); 2.48 (*m*, H–C(6)); 2.58 (*m*, H–C(9)); 3.18 (*s*, H–C(16)); 4.63 (*d*, *J* = 7.6, H–C(3)); 4.82 (*dd*, *J* = 5.2, 7.6 Hz, H–C(2)); 5.67 (*s*, H–C(17)). ^{13}C-NMR (125 MHz, CDCl3): 20.3 (*t*, C(14)); 22.9 (*q*, C(19)); 25.4 (*t*, C(10)); 25.9 (*q*, C(18)); 28.2 (*q*, C(20)); 28.9 (*t*, C(6)); 31.9 (*t*, C(13)); 33.5 (*t*, C(9)); 34.0 (*d*, C(1)); 35.2 (*t*, C(5)); 38.2 (*s*, C(12)); 43.1 (*s*, C(4)); 45.3 (*t*, C(11)); 54.9 (*d*, C(16)); 78.4 (*d*, C(2)); 82.0 (*d*, C(3)); 134.2 (*s*, C(8)); 134.4 (*s*, C(15)); 136.3 (*s*, C(7)); 138.3 (*d*, C(17)); 154.7 (*s*, C=O). Anal. calc. for $C_{21}H_{28}O_3$: C 76.79, H 8.59; found: C 76.49, H 8.59.

Trinervita-7,11,15(17)-triene-2α,3α-diol Carbonate (**17**). A mixture of **8** (145 mg, 0.48 mmol) and 1,1′-carbonyldiimidazole (311 mg, 1.92 mmol) in benzene (10 ml) was stirred at 20° for 1 h, and the mixture was diluted with H_2O (10 ml), and then extracted with Et_2O (3 × 15 ml). The org. phase was dried (Na_2SO_4) and evaporated, and the residue was purified by CC (hexane/$CHCl_3$ 2:1): 145 mg (92%) of **17**. Colorless prisms. M.p. 211–213° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.23 (*s*, Me(18)); 1.45–1.55 (*m*, 2 H–C(6), H–C(14)); 1.51 (*s*, Me(20)); 1.65 (*s*, Me(19)); 1.74 (br. *d*, *J* = 12.2, H–C(9)); 1.86 (*dt*, *J* = 4.0, 12.8, H–C(5)); 1.94 (*tt*, *J* = 5.0, 13.0, H–C(10)); 2.06 (*dddd*, *J* = 3.4, 10.4, 10.8, 14.1, a H–C(14)); 2.12 (*dddd*, *J* = 2.8, 4.9, 11.5, 12.8, H–C(10)); 2.12 (*dd*, *J* = 4.0, 10.4, H–C(1)); 2.18 (*td*, *J* = 1.8, 12.6, H–C(5)); 2.46 (*m*, H–C(13)), 2.51 (*dt*, *J* = 8.6, 16.5, H–C(13)); 2.58 (*dt*, *J* = 4.9, 12.5, H–C(9)), 3.13 (*s*, H–C(16)); 4.51 (*d*, *J* = 8.0, H–C(3)); 4.84 (br. *dd*, *J* = 4.9, 12.0, H–C(11)); 4.85 (*dd*, *J* = 4.0, 8.0, H–C(2)); 4.99 (*s*, H–C(17)); 5.00 (*s*, H–C(17)). ^{13}C-NMR (125 MHz, $CDCl_3$): 15.5 (*q*, C(20)); 19.4 (*q*, C(19)); 23.2 (*t*, C(10)); 23.9 (*t*, C(14)); 26.2 (*q*, C(18)); 29.3 (*t*, C(13)); 31.8 (*t*, C(9)); 36.1 (*t*, C(6)); 40.5 (*t*, C(5)); 40.6 (*d*, C(1)); 47.4 (*s*, C(4)); 57.5 (*d*, C(16)); 81.3 (*d*, C(2)); 81.5 (*d*, C(3)); 112.3 (*t*, C(17)); 124.7 (*d*, C(11)); 131.0 (*s*, C(8)); 132.8 (*s*, C(8)); 136.2 (*s*, C(12)); 145.8 (*s*, C(15)); 155.0 (*s*, C=O). Anal. calc. for $C_{21}H_{28}O_3$: C 76.79, H 8.59; found: C 76.53, H 8.75.

Trinervita-7,15(17)-diene-2α,3α-diol Carbonate (**18a** and **18b**). A soln. of **17** (100 mg, 0.30 mmol) in CH_2Cl_2 (4 ml) was vigorously stirred under a balloon filled with H_2 for 30 h in the presence of PtO_2 (27 mg, 0.12 mmol), and the mixture was filtered through a pad of SiO_2 (3 g), and SiO_2 was washed with CH_2Cl_2 (20 ml). The filtrate was evaporated, and the residue was purified by CC (hexane/AcOEt 8:1): 99 mg of a white solid. The solid was separated by HPLC (μ-*Porasil* column (7.8 × 300 mm), hexane/AcOEt 30:1, flow 3 ml/min, RI detector): 84 mg (85%) of **18a** and 15 mg (15%) of **18b**.

Data of **18a**. Colorless prisms. M.p. 188–189° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.81 (*d*, *J* = 6.4, Me(20)), 0.82–0.91 (*m*, H–C(11)); 1.25 (*s*, Me(18)); 1.25–1.47 (*m*, H–C(10); 2 H–C(13)); 1.49–1.61 (*m*, 2 H–C(5), H–C(10), H-(14)); 1.63 (*s*, Me(19)); 1.64–1.70 (*m*, H–C(9), H–C(12)); 1.78 (br. *t*, *J* = 10.3, H–C(11)); 2.02 (*m*, H–C(14)); 2.35 (*dd*, *J* = 3.7, 7.9, H–C(1)); 2.41 (*m*, H–C(6)); 2.52 (*dd*, *J* = 8.1, 16.3, H–C(6)); 2.92 (*dt*, *J* = 2.6, 13.0, H–C(9)); 3.20 (*s*, H–C(16)), 4.50 (*d*, *J* = 7.8, H–C(3)); 4.84 (*dd*, *J* = 3.8, 7.8, H–C(2)); 5.26 (*s*, H–C(17)); 5.34 (*s*, H–C(17)). ^{13}C-NMR (125 MHz, $CDCl_3$): 19.3 (*q*, C(19)); 21.6 (*t*, C(10)); 21.9 (*q*, C(20)); 22.5 (*t*, C(14)); 26.3 (*q*, C(18)); 28.0 (*d*, C(12)); 29.7 (*t*, C(6)); 33.1 (*t*, C(9)); 34.0 (*t*, C(11)); 36.0 (*t*, C(13)); 36.5 (*t*, C(5)); 38.8 (*d*, C(1)); 48.1 (*s*, C(4)); 58.0 (*d*, C(16)); 81.1 (*d*, C(2)); 81.7 (*d*, C(3)); 114.9 (*t*, C(17)); 133.4 (*s*, C(8)); 136.0 (*s*, C(7)); 147.0 (*s*, C(15)); 155.1 (*s*, C=O). Anal. calc. for $C_{21}H_{30}O_3$: C 76.33, H 9.15; found: C 75.90, H 9.42.

Data of **18b**. Colorless prisms. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.82 (*d*, *J* = 6.7, Me(20)); 0.85–0.94 (*m*, H–C(11)); 1.04 (br. *t*, *J* = 12.1, H–C(11)); 1.13–1.27 (*m*, H–C(10), H–C(13)); 1.25 (*s*, Me(18)); 1.47 (*ddd*, *J* = 3.1, 7.6, 12.5, H–C(5)); 1.49–1.63 (*m*, H–C(5), H–C(9), H–C(10), H–C(12), H–C(13), H–C(14)); 1.57 (*s*, Me(19)), 2.06 (*m*, H–C(14)); 2.40 (*m*, H–C(1)); 2.49 (*m*, 2 H–C(6)); 2.90 (*dt*, *J* = 4.9, 12.1, H–C(9)); 3.20 (*s*, H–C(16)); 4.50 (*d*, *J* = 7.3, H–C(3)); 4.78 (*dd*, *J* = 4.0, 7.3, H–C(2)); 5.31 (*s*, 2 H–C(17)). ^{13}C-NMR (125 MHz, $CDCl_3$): 19.2 (*q*, C(19)); 22.9 (*q*, C(20)); 23.0 (*t*, C(10)); 24.8 (*t*, C(14)); 25.6 (*q*, C(18)); 29.6 (*t*, C(6)); 30.3 (*t*, C(9)); 30.6 (*d*, C(12)); 34.7 (*t*, C(11)); 36.5 (*t*, C(5)); 37.2 (*t*, C(13)); 39.8 (*d*, C(1)); 47.7 (*s*, C(4)); 58.2 (*d*, C(16)); 81.4 (*d*, C(3)); 81.9 (*d*, C(2)); 114.9 (*t*, C(17)); 131.8 (*s*, C(8)); 136.3 (*s*, C(7)); 145.7 (*s*, C(15)); 155.0 (*s*, C=O). Anal. calc. for $C_{21}H_{30}O_3$: C 76.33, H 9.15; found: C 76.15, H 9.27.

Trinervita-7,15(17)-diene-2α,3α-diol (**15a** and **15b**). A soln. of **18a** (60 mg, 0.18 mmol) in 2M KOH/MeOH (6 ml) was stirred at 20° for 6 h, and then diluted with H_2O (20 ml). The mixture was extracted with Et_2O

(3×20 ml) and the org. phase was washed with brine (2×5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 8:1): 55 mg (99%) of **15a**. As described for **15a**, with **18b** (20 mg, 0.06 mmol): 18 mg (99%) of **15b** after CC.

Data of **15a**. Colorless prisms. M.p. 120–121° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.91 (*d, J* = 6.4, Me(20)); 0.98 (*s*, Me(18)); 1.16 (*td, J* = 10.5, 12.8, H–C(5)); 1.21–1.37 (*m*, OH–C(2), H–C(11), H–C(13), H–C(14)); 1.42–1.57 (*m*, 2 H–C(10), H–C(11), H–C(12), H–C(13)); 1.54 (*s*, Me(19)); 1.61 (br. *d, J* = 14.6, H–C(9)); 2.056 (*dt, J* = 6.7, 13.4, H–C(14)); 2.059 (*ddd, J* = 3.1, 7.0, 12.8, H–C(5)); 2.23 (br. *s*, OH–C(3)), 2.34–2.43 (*m*, 2 H–C(6)); 2.88 (*s*, H–C(16)), 2.92 (*d, J* = 13.4, H–C(1)); 3.00 (*ddd, J* = 5.8, 11.0, 14.6, H–C(9)); 3.33 (br. *s*, H–C(3)); 3.72 (br. *s*, H–C(2)); 4.93 (*s*, H–C(17)); 5.22 (*s*, H–C(17)). ^{13}C-NMR (125 MHz, $CDCl_3$): 17.9 (*q*, C(19)); 20.0 (*t*, C(10)); 20.8 (*q*, C(18)); 23.8 (*q*, C(20)); 29.0 (*t*, C(14)); 29.5 (*t*, C(6), C(13)); 30.9 (*t*, C(11)); 31.4 (*t*, C(9)); 35.5 (*d*, C(12)); 36.5 (*t*, C(5)); 40.7 (*d*, C(1)); 51.4 (*s*, C(4)); 61.4 (*d*, C(16)); 72.2 (*d*, C(3)); 78.0 (*d*, C(2)); 111.6 (*t*, C(17)); 129.5 (*s*, C(8)); 136.4 (*s*, C(7)); 147.2 (*s*, C(15)). Anal. calc. for $C_{20}H_{32}O_2$: C 78.90, H 10.59; found: C 78.84, H 10.70.

Data of **15b**. Colorless needles. M.p. 127–128° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.88 (*d, J* = 6.7, Me(20)); 0.98 (*s*, Me(18)); 1.09 (*dddd, J* = 2.0, 7.6, 12.8, 16.4, H–C(11)); 1.15 (*td, J* = 10.5, 12.6, H–C(5)); 1.17–1.26 (*m*, H–C(11)); 1.22 (br. *d, J* = 7.8, OH–C(2)); 1.34 (*dddd, J* = 3.0, 5.0, 11.0, 14.0, H–C(13)); 1.4–1.48 (*m*, H–C(10), H–C(14)); 1.49–1.58 (*m*, H–C(9), H–C(10), H–C(13)); 1.56 (*s*, Me(19)); 1.67–1.77 (*m*, H–C(12)); 1.94 (*dtd*, *J* = 3.0, 10.7, 14.0, H–C(14)); 2.05 (*ddd, J* = 3.4, 5.8, 12.6, H–C(5)); 2.19 (br. *s*, OH–C(3)); 2.38 (br. *d, J* = 10.1, 2 H–C(6)); 2.61 (*d, J* = 10.7, H–C(1)); 2.95 (*s*, H–C(16)); 2.97 (*dt, J* = 7.7, 11.3, H–C(9)); 3.34 (br. *s*, H–C(3)); 3.73 (*td, J* = 2.6, 7.8, H–C(2)); 5.13 (*s*, H–C(17)); 5.24 (*s*, H–C(17)). ^{13}C-NMR (125 MHz, $CDCl_3$): 18.5 (*q*, C(19)); 21.1 (*q*, C(18)); 22.7 (*q*, C(20)); 24.9 (*t*, C(10)); 25.6 (*t*, C(14)); 29.8 (*t*, C(6)); 30.7 (*t*, C(9)); 30.9 (*d*, C(12)); 33.1 (*t*, C(13)); 35.2 (*t*, C(11)); 36.7 (*t*, C(5)); 42.8 (*d*, C(1)); 51.2 (*s*, C(4)); 61.6 (*d*, C(16)); 72.1 (*d*, C(3)); 78.9 (*d*, C(2)); 112.5 (*t*, C(17)); 130.2 (*s*, C(8)); 135.5 (*s*, C(7)); 148.7 (*s*, C(15)). Anal. calc. for $C_{20}H_{32}O_2$: C 78.90, H 10.59; found: C 78.69, H 10.87.

3α-(Methoxymethoxy)trinervita-7,15(17)-dien-2α-ol (**19**). A mixture of **15a** (300 mg, 0.99 mmol), EtN(i-Pr)$_2$ (0.69 ml, 3.96 mmol), $ClCH_2OMe$ (0.15 ml, 1.98 mmol) in CH_2Cl_2 (10 ml) was stirred at 20° for 5 h, and then H_2O (10 ml) and sat. aq. NH_4Cl soln. (5 ml) were added. The mixture was extracted with Et_2O (3×15 ml), the org. phase was washed with brine (3×5 ml), dried (Na_2SO_4), and evaporated, and the residue was purified by CC (hexane/AcOEt 40:1 → 4:1): 254 mg (74%) of **19**, 45 mg (13%) of **20**, 27 mg (7 %) of **21** and 15 mg of recovered **15a**.

Data of **19**. Colorless gum. IR (CCl_4): 3612, 2932, 2868, 1454, 1378, 1154, 1036. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.91 (*d, J* = 6.7, Me(20)); 1.07 (*s*, Me(18)); 1.15 (*td, J* = 10.7, 12.5, H–C(5)); 1.23–1.35 (*m*, H–C(11), H–C(13), H–C(14)); 1.42–1.70 (*m*, H–C(9), 2 H–C(10), H–C(11), H–C(12), H–C(13)); 1.52 (*s*, Me(19)); 1.97 (*ddd, J* = 1.9, 7.0, 12.9, H–C(5)); 2.14 (*dt, J* = 6.4, 14.0, H–C(14)); 2.32–2.43 (*m*, 2 H–C(6)); 2.78 (br. *d, J* = 12.5, H–C(1)); 2.85 (*s*, H–C(16)); 3.08 (*ddd, J* = 5.2, 10.1, 13.1, H–C(9)); 3.41 (br. *s*, H–C(3)); 3.44 (*s*, *Me*OCH$_2$O); 3.88 (br. *s*, H–C(2)); 4.65, 4.81 (2 *d, J* = 6.7, MeO*CH*$_2$O); 4.93 (*s*, H–C(17)); 5.18 (*s*, H–C(17)). ^{13}C-NMR (125 MHz, $CDCl_3$): 17.8 (*q*, C(19)); 20.4 (*t*), 21.1 (*q*, C(18)); 23.9 (*q*, C(20)); 29.2 (*t*), 29.3 (*t*), 29.7 (*t*), 31.0 (*t*), 31.1 (*t*), 35.7 (*d*, C(12)); 36.1 (*t*), 39.9 (*d*, C(1)); 50.9 (*s*, C(4)); 55.7 (*q*, *Me*OCH$_2$O); 61.9 (*d*, C(16)); 75.3 (*d*, C(3)); 78.3 (*d*, C(2)); 96.0 (*t*, MeO*CH*$_2$O); 111.4 (*t*, C(17)); 129.4 (*s*, C(8)); 136.0 (*s*, C(7)); 146.3 (*s*, C(15)). HR-MS: 348.2654 ($C_{22}H_{36}O_3^+$; calc. 348.2664).

Data of **20**. Colorless gum. IR (CCl_4): 3476, 2928, 1456, 1378, 1146, 1038. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.91 (*d, J* = 7.2, Me(20)); 1.00 (*s*, Me(18)); 1.54 (*s*, Me(19)); 3.36 (*d, J* = 1.8, H–C(3)); 3.43 (*s*, *Me*OCH$_2$O); 3.60 (br. *s*, H–C(2)); 4.50, 4.73 (2 *d, J* = 7.2, MeO*CH*$_2$O); 4.84 (*s*, H–C(17)); 5.10 (*s*, H–C(17)). HR-MS: 348.2648 ($C_{22}H_{36}O_3^+$; calc. 348.2664).

Data of **21**. Colorless prisms. M.p. 65–67° (MeOH). IR (CCl_4): 2932, 1454, 1378, 1152, 1032. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.91 (*d, J* = 7.0, Me(20)); 1.09 (*s*, Me(18)); 1.15 (*td, J* = 10.7, 12.8, H–C(5)); 1.20–1.32 (*m*, H–C(11), H–C(13), H–C(14)); 1.39–1.50 (*m*, H–C(10), H–C(11), H–C(12)); 1.51 (*d, J* = 1.0, Me(19)); 1.52–1.65 (*m*, H–C(9), H–C(10), H–C(13)); 1.99 (*ddd, J* = 2.2, 7.3, 12.8, H–C(5)); 2.13 (*dt, J* = 5.8, 13.5, H–C(14)); 2.34–2.42 (*m*, 2 H–C(6)); 2.66 (*d, J* = 12.5, H–C(1)); 2.85 (*s*, H–C(16)); 3.14 (*ddd, J* = 5.2, 11.0, 13.1, H–C(9)); 3.36 (*s*, *Me*OCH$_2$O); 3.43 (*d, J* = 3.0, H–C(3)); 3.45 (*s*, *Me*OCH$_2$O); 3.84 (*t, J* = 3.0, H–C(2)); 4.53 (*d, J* = 6.7, MeO*CH*$_2$O); 4.54 (*d, J* = 7.0, MeO*CH*$_2$O); 4.77 (*d, J* = 6.7, MeO*CH*$_2$O); 4.85 (*s*, H–C(17)); 4.86 (*d, J* = 7.0, MeO*CH*$_2$O); 5.12 (*s*, H–C(17)). ^{13}C-NMR (125 MHz, $CDCl_3$): 18.1 (*q*, C(19)); 20.4 (*q*, C(18)); 20.8 (*t*, C(10)); 24.3 (*q*, C(20)); 29.4 (*t*, C(6)); 29.7 (*t*, C(13)); 30.0 (*t*, C(14)); 30.8 (*t*, C(9)); 31.4 (*t*, C(11)); 35.7 (*t*, C(5)); 36.0 (*d*, C(12)); 40.0 (*d*, C(1)); 51.1 (*s*, C(4)); 55.5, 56.1 (2 × *q*, *Me*OCH$_2$O); 62.2 (*d*, C(16)); 77.4 (*d*, C(3)); 80.5 (*d*, C(2)); 95.2, 97.2 (2 *t*, MeO*CH*$_2$O); 111.0 (*t*, C(17)); 129.4 (*s*, C(8)); 136.4 (*s*, C(7)); 146.2 (*s*, C(15)). HR-MS: 392.2931 ($C_{24}H_{40}O_4^+$; calc. 392.2927).

3α-(Methoxymethoxy)trinervita-7,15(17)-dien-2-one (**22**). A soln. of **19** (254 mg, 0.73 mmol) in CH_2Cl_2 (4 ml) was added to the mixture of pyridinium chlorocromate (PCC; 520 mg, 2.41 mmol), AcONa (902 mg, 11.0 mmol) and, molecular sieves (4 Å; 520 mg) in CH_2Cl_2 (4 ml) at 20° with vigorous stirring. After vigorous stirring at 20° for 5 h, Et_2O (30 ml) was added and then passed through a pad of SiO_2 (8 g). The pad was washed with Et_2O (5 × 8 ml). The combined filtrate was evaporated, and the residue was purified by CC (hexane/AcOEt 15:1): 230 mg (91%) of **22**. Colorless needles. M.p. 116–118° (hexane). IR (CCl_4): 2936, 1734, 1644, 1156, 1120, 1038. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89 (*d, J* = 6.4, Me(20)); 1.23 (*s*, Me(18)); 1.52 (*s*, Me(19)); 2.94 (*d, J* = 12.0, H–C(1)); 3.08 (*td, J* = 8.5, 14.7, H–C(9)); 3.14 (br. *s*, H–C(16)); 3.34 (*s*, *Me*OCH$_2$O); 4.07 (*s*, H–C(3)); 4.47, 4.57 (*d, J* = 7.1, MeOC*H*$_2$O); 5.12 (*s*, H–C(17)); 5.33 (*s*, H–C(17)). ^{13}C-NMR (100 MHz, $CDCl_3$): 17.9 (*q*, C(19)); 18.6 (*q*, C(18)); 21.2 (*t*), 23.7 (*t*), 24.1 (*q*, C(20)); 29.0 (*t*), 29.1 (*t*), 31.1 (*t*), 31.7 (*t*), 34.3 (*t*), 35.7 (*d*, C(12)); 50.0 (*d*, C(1)); 52.7 (*s*, C(4)); 56.0 (*q*, *Me*OCH$_2$O); 61.8 (*d*, C(16)); 80.6 (*d*, C(3)); 96.1 (*t*, MeO*C*H$_2$O); 111.3 (*t*, C(17)); 130.7 (*s*, C(8)); 134.7 (*s*, C(7)); 145.4 (*s*, C(15)); 206.5 (*s*, C(2)). Anal. calc. for $C_{22}H_{34}O_3$: C 76.26, H 9.89; found: C 75.06, H 10.22.

2α-(Methoxymethoxy)trinervita-7,15(17)-dien-3-one (**23**). As described for **22**, with **20** (40 mg, 0.11 mmol): 33 mg (85%) of **23** after CC. Colorless prisms. M.p. 93–95° (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (*s*, Me(18)); 0.92 (*d, J* = 6.4, Me(20)); 1.59 (*s*, Me(19)); 3.66 (*d, J* = 12.4, H–C(1)); 16)); 3.06 (*ddd, J* = 5.9, 9.0, 13.9, H–C(9)); 3.44 (*s*, *Me*OCH$_2$O); 3.78 (*d, J* = 3.6, H–C(2)); 4.64, 4.72 (2 *d, J* = 7.1, MeOC*H*$_2$O); 4.88 (*s*, H–C(17)); 5.07 (*s*, H–C(17)). ^{13}C-NMR (100 MHz, $CDCl_3$): 18.0 (*q*, C(19)); 19.8 (*t*, C(10)); 23.5 (2*q*, C(18), C(20)); 28.0 (*t*, C(14)); 30.0 (*t*, C(13)); 30.5 (*t*, C(6)); 30.9 (*t*, C(11)); 31.2 (*t*, C(9)); 34.5 (*d*, C(12)); 34.7 (*t*, C(5)); 41.0 (*d*, C(1)); 55.9 (*q*, *Me*OCH$_2$O); 59.5 (*s*, C(4)); 62.0 (*d*, C(16)); 84.7 (*d*, C(2)); 95.1 (*t*, MeO*C*H$_2$O); 113.3 (*t*, C(17)); 130.2 (*s*, C(8)); 135.9 (*s*, C(7)); 144.9 (*s*, C(15)); 211.7 (*s*, C(3)). Anal. calc. for $C_{22}H_{34}O_3$: C 76.26, H 9.89; found: C 6.17, H 10.19.

3α-(Methoxymethoxy)trinervita-1(15),7-dien-2-one (**24**). A soln. of **22** (230 mg, 0.66 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.39 ml, 2.6 mmol) in toluene (9 ml) was heated under reflux for 7 d. The sat. aq. NH_4Cl soln. (5 ml) and H_2O (10 ml) were added at 20°. The mixture was extracted with Et_2O (3 × 10 ml), the org. phase was washed with brine (3 × 4 ml), dried (Na_2SO_4) and evaporated, and the residue was purified by CC (hexane/AcOEt 15:1): 205 mg (89%) of **24**. Colorless prisms. M.p. 98–99° (MeOH). IR (CCl_4): 2932, 1674, 1632, 1378, 1156, 1038. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.84 (*d, J* = 6.8, Me(20)); 0.94–1.05 (*m*, H–C(11)); 1.01 (*s*, Me(18)); 1.08–1.17 (*m*, H–C(11)); 1.18–1.29 (*m*, H–C(10)); 1.31–1.41 (*m*, H–C(13)); 1.36 (*ddd, J* = 9.0, 11.0, 13.2, H–C(5)); 1.46–1.60 (*m*, H–C(10), H–C(12), H–C(13)); 1.58 (*s*, Me(19)); 1.67–1.77 (*m*, H–C(9)); 2.03 (*ddd, J* = 2.4, 8.8, 13.2, H–C(5)); 2.14 (*s*, Me(17)); 2.15 (*ddd, J* = 3.2, 4.8, 13.2, H–C(14)); 2.29 (*ddd, J* = 5.9, 10.0, 13.4, H–C(9)); 2.33–2.45 (*m*, H–C(6)); 2.45 (*td, J* = 8.6, 17.6, H–C(6)); 2.64 (*s*, H–C(16)); 2.91 (*dt, J* = 3.4, 13.2, H–C(14)); 3.46 (*s*, *Me*OCH$_2$O); 4.06 (*s*, H–C(3)); 4.79, 4.92 (2*d, J* = 7.1 Hz, MeOC*H*$_2$O). ^{13}C-NMR (100 MHz, $CDCl_3$): 18.3 (*q*, C(18)); 19.2 (*q*, C(19)); 22.1 (*t*, C(10)); 23.1 (*t*, C(14)); 23.3 (*q*, C(20)); 24.8 (*q*, C(17)); 29.0 (*t*, C(6)); 30.0 (*t*, C(11)); 31.2 (*t*, C(13)); 32.8 (*t*, C(5)); 33.0 (*d*, C(12)); 33.6 (*t*, C(9)); 53.6 (*s*, C(4)); 56.0 (*q*, *Me*OCH$_2$O); 59.8 (*d*, C(16)); 79.5 (*d*, C(3)); 97.8 (*t*, MeO*C*H$_2$O); 128.7 (*s*, C(1)); 136.0 (*s*, C(7)); 136.1 (*s*, C(8)); 154.0 (*s*, C(15)); 197.3 (*s*, C(2)). HR-MS: 346.2518 ($C_{22}H_{34}O_3^+$; calc. 346.2508). Anal. calc. for $C_{22}H_{34}O_3$: C 76.26, H 9.89; found: C 76.14, H 10.02.

7-Hydroxy-3α-(methoxymethoxy)trinervita-1(15)-en-2-one (**29**). A soln. of 1.0M $BH_3 \cdot THF$ (0.3 ml, 0.3 mmol) was added to a soln. of **24** (66 mg, 0.19 mmol) in THF (2 ml), and the mixture was stirred at 25° for 4 h. 3M aq. NaOH (1 ml) and 33% aq. H_2O_2 (1 ml) were added to the mixture at 0°, and the mixture was stirred at 25° for 2 h, H_2O (10 ml) was then added, and the mixture was extracted with Et_2O (3 × 10 ml), the org. phase was washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue was purified by CC (hexane/AcOEt 5:1): 44.3 mg (94% yield) of **29** and 18.8 mg of recovered **24**. Colorless gum. ^{1}H-NMR (270 MHz, $CDCl_3$): 0.84–1.04 (*m*, Me(19), Me(20)); 1.11 (*s*, Me(18)); 2.19 (*s*, Me(17)); 2.75–2.90 (*m*, H–C(14)); 2.97 (*s*, H–C(16)); 3.45 (*s*, *Me*OCH$_2$O); 4.42 (*s*, H–C(3)); 4.76, 4.86 (2 *d, J* = 7.3, MeOC*H*$_2$O).

3α-(Methoxymethoxy)-7,8-epoxytrinervita-1(15)-en-2-one (**31b**). *m*-CPBA (28 mg, 0.17 mmol) was added to an ice-cooled soln. of **24** (52 mg, 0.15 mmol) in CH_2Cl_2 (3 ml), and the mixture was stirred at 0° for 1 h. Sat. aq. $NaHCO_3$ soln. (2 ml) and H_2O (7 ml) were added, and the mixture was extracted with Et_2O (3 × 10 ml), and the org. phase was washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated. The residue was purified by CC (hexane/AcOEt 10:1): 54 mg (99%) of **31b**. Colorless gum.^{1}H-NMR (300 MHz, $CDCl_3$): 0.87 (*d, J* = 7.1, Me(20)); 1.00 (*s*, Me(18)); 1.23 (*s*, Me(19)); 1.99 (*s*, Me(17)); 2.67 (*s*, H–C(16)); 3.44 (*s*, *Me*OCH$_2$O); 4.19 (*s*, H–C(3)); 4.75, 4.94 (2 *d, J* = 7.2, MeOC*H*$_2$O). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.7 (*q*, C(18)); 22.8 (*q*, C(19)); 22.9 (*t*, C(14)); 24.2 (*q*, C(17)); 25.7 (*q*, C(20)); 26.7 (*t*), 29.6 (*t*), 32.5 (*t*), 33.9 (*t*), 34.7 (*t*), 35.4 (*d*, C(12)); 37.9 (*t*), 52.1 (*s*, C(4)), 56.0 (*q*, *Me*OCH$_2$O); 58.0 (*d*, C(16)); 67.0 (*s*, C(7)); 75.9 (*s*, C(8)); 78.1 (*d*, C(3)); 97.2 (*t*, MeO*C*H$_2$O); 136.7 (*s*, C(1)); 150.2 (*s*, C(15)); and 197.5 (*s*, C(2)). HR-MS: 362.2464 ($C_{22}H_{34}O_4^+$; calc. 362.2457).

3α-Hydroxytrinervita-1(15),7-dien-2-one (**25**). A soln. of **24** (143 mg, 0.41 mmol) in 2M HCl/MeOH (5 ml) was stirred at 20° for 14 h, and sat. aq. $NaHCO_3$ soln. (10 ml) was added. The mixture was extracted with Et_2O (3 × 10 ml), and the combined org. extract was washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue was purified by CC (hexane/AcOEt 20:1): 106 mg (85%) of **25**. Colorless prisms. M.p. 80–82° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86 (*d, J* = 7.0, Me(20)); 0.92 (*s*, Me(18)); 0.98–1.04 (*m*, H–C(11)); 1.14–1.24 (*m*, H–C(10), H–C(11)); 1.30–1.44 (*m*, H–C(12), H–C(13)); 1.40 (*ddd, J* = 8.6, 11.3, 13.4, H–C(5)); 1.51–1.64 (*m*, H–C(10), H–C(13)); 1.57 (*s*, Me(19)); 1.69–1.76 (*m*, H–C(9)); 2.12 (*ddd, J* = 2.5, 9.2, 13.5, H–C(5)); 2.16 (*s*, Me(17)); 2.24 (*ddd, J* = 3.1, 4.9, 14.1, H–C(14)); 2.29 (*ddd, J* = 6.5, 9.2, 14.1, H–C(9)); 2.38 (br. *dd, J* = 11.3, 16.8, H–C(6)); 2.53 (*td, J* = 8.6, 16.8, H–C(6)); 2.68 (*s*, H–C(16)); 2.90 (*ddd, J* = 3.4, 12.5, 14.1, H–C(14)); 3.58 (*d, J* = 2.2, OH–C(3)); 4.16 (*d, J* = 2.2, H–C(3)). ^{13}C-NMR (125 MHz, $CDCl_3$): 17.4 (*q*, C(18)); 19.3 (*q*, C(19)); 22.7 (*t*, C(10)); 23.2 (*t*, C(14)); 23.4 (*q*, C(20)); 24.9 (*q*, C(17)); 29.0 (*t*, C(6)); 30.5 (*t*, C(11)); 31.4 (*t*, C(13)); 32.7 (*t*, C(5)); 33.2 (*d*, C(12)); 33.6 (*t*, C(9)); 55.1 (*s*, C(4)); 59.3 (*d*, C(16)); 74.8 (*d*, C(3)); 128.5 (*s*, C(1)); 134.4 (*s*, C(7)); 135.5 (*s*, C(8)); 156.1 (*s*, C(15)); 199.1 (*s*, C(2)). HR-MS: 302.2241 ($C_{20}H_{30}O_2^+$; calc. 302.2246).

2-Oxotrinervita-1(15),7-dien-3α-ol Acetate (**26**). AcCl (66 ml, 0.70 mmol) was added to a stirred mixture of **25** (106 mg, 0.35 mmol) and pyridine (85 µl, 1.05 mmol) in CH_2Cl_2 (3 ml) at 25°. After addition of DMAP (5 mg, 0.04 mmol), the mixture was stirred at 25° for 1 h. MeOH (0.5 ml) and H_2O (10 ml) were added, the mixture was extracted with Et_2O (3 × 15 ml), and the combined org. extract was washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue was purified by CC (hexane/AcOEt 10:1): 120 mg (100%) of **26**. Colorless prisms. M.p. 138–140° (hexane). IR (CCl_4): 2932, 2868, 1750, 1680, 1456, 1382, 1232, 1038. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.84 (*d, J* = 7.1, Me(20)); 1.00–1.08 (*m*, H–C(11)); 1.04 (*s*, Me(18)); 1.11–1.34 (*m*, H–C(10), H–C(11), H–C(13)); 1.38 (*ddd, J* = 8.8, 11.0, 13.4, H–C(5)); 1.42–1.58 (*m*, H–C(10), H–C(12), H–C(13)); 1.60 (*s*, Me(19)); 1.68–1.75 (*m*, H–C(9)); 1.73 (*ddd, J* = 2.4, 9.3, 13.4, H–C(5)); 2.13–2.22 (*m*, H–C(14)); 2.16 (*s*, Ac); 2.19 (*s*, Me(17)); 2.29 (*ddd, J* = 6.1, 9.5, 13.2, H–C(9)); 2.35 (br. *dd, J* = 11.0, 17.1, H–C(6)); 2.52 (*td, J* = 9.0, 17.1, H–C(6)); 2.70 (br. *s*, H–C(16)); 2.89 (*dt, J* = 3.2, 13.2, H–C(14)); 5.45 (*s*, H–C(3)). ^{13}C-NMR (125 MHz, $CDCl_3$): 18.6 (*q*, C(18)); 19.5 (*q*, C(19)); 20.8 (*q*, *Me*CO); 22.6 (*t*, C(10)); 23.3 (*t*, C(14)); 23.5 (*q*, C(20)); 24.9 (*q*, C(17)); 28.9 (*t*, C(6)); 30.3 (*t*, C(11)); 31.5 (*t*, C(13)); 33.0 (*t*, C(5)); 33.1 (*d*, C(12)); 33.8 (*t*, C(9)); 52.8 (*s*, C(4)); 59.8 (*d*, C(16)); 76.1 (*d*, C(3)); 129.6 (*s*, C(1)); 135.4 (*s*, C(7)); 135.9 (*s*, C(8)); 154.5 (*s*, C(15)); 170.9 (*s*, Me*C*O); 192.9 (*s*, C(2)). Anal. calc. for $C_{22}H_{32}O_3$: C 76.70, H 9.36; found: C 76.60, H 9.62.

2-Oxo-7α,8α-epoxytrinervita-1(15)-en-3α-ol Acetate (**31a**). *m*-CPBA (66 mg, 0.38 mmol) was added to an ice-cooled soln. of **26** (120 mg, 0.35 mmol) in CH_2Cl_2 (4 ml), and the mixture was stirred at 0° for 1 h, and then a sat. aq. $NaHCO_3$ soln. (2 ml) and H_2O (5 ml) were added. The mixture was extracted with Et_2O (3 × 15 ml), and the org. phase was washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated. The residue was purified by CC (hexane/AcOEt 10:1): 125 mg (100%) of **31a**. Colorless prisms. M.p. 136–138° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.88 (*d, J* = 7.1, Me(20)); 1.08 (*s*, Me(18)); 1.24 (*s*, Me(19)); 2.05 (*s*, Me(17)); 2.23 (*s*, Ac); 2.76 (br. *s*, H–C(16)); 2.87 (*dt, J* = 3.4, 13.7, H–C(14)); 5.52 (*s*, H–C(3)). ^{13}C-NMR (125 MHz, $CDCl_3$): 19.4 (*q*, C(18)); 20.6 (*q*, *Me*CO); 21.7 (*q*, C(19)); 23.16 (*t*, C(14)); 23.23 (*q*, C(17)); 25.9 (*q*, C(20)); 26.6 (*t*), 28.7 (*t*), 32.3 (*t*), 34.5 (*t*), 34.8 (*t*), 35.3 (*d*, C(12)); 36.2 (*t*), 50.2 (*s*, C(4)); 58.2 (*d*, C(16)); 68.0 (*s*, C(7)); 75.6 (*s*, C(8)); 76.3 (*d*, C(3)); 134.6 (*s*, C(1)); 152.8 (*s*, C(15)); 170.9 (*s*, Me*C*O); 193.3 (*s*, C(2)). HR-MS: 360.2310 ($C_{22}H_{32}O_4^+$; calc. 360.2301).

2-Oxotrinervita-1(15),6-diene-3α,8α-diol 3α-Acetate (**30a**). Under N_2, TMSCl (0.085 ml, 0.67 mmol) was added to a soln. of **31a** (80 mg, 0.22 mmol) in CH_2Cl_2 (3 ml) at −10°, and the mixture was stirred at −10° for 48 h. A sat. aq. $NaHCO_3$ soln. (5 ml) was added, and the mixture was extracted with Et_2O (3 × 15 ml). The combined org. extract was washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated. The residue was purified by CC (hexane/AcOEt 12:1 → 3:1): 32.8 mg (41%) of **30a**, 22.4 mg (28%) of *2-oxotrinervita-1(15),8(19)-diene-3α,7α-diol 3α-Acetate* **32**, and 8 mg of recovered **31a**.

Data of **30a**. Colorless prisms. M.p. 202–204° (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.79–0.94 (*m*, H–C(10), H–C(11), H–C(13)); 0.87 (br. *s*, Me(20)); 1.18 (*s*, Me(18)); 1.29–1.45 (*m*, H–C(9), H–C(11), H–C(12)); 1.44 (*s*, Me(19)); 1.57 (*dddd, J* = 2.2, 5.1, 7.3, 13.7, H–C(10)); 1.69 (*dt, J* = 3.4, 13.9, H–C(13)); 2.05 (br. *d, J* = 12.2, H–C(9)); 2.07 (*ddd, J* = 1.7, 3.6, 16.1, H–C(5)); 2.13 (*td, J* = 3.4, 13.9, H–C(14)); 2.20 (*dd, J* = 3.2, 16.1, H–C(5)); 2.21 (*s*, Ac); 2.35 (*s*, Me(17)); 2.91 (*dt, J* = 3.9, 13.9, H–C(14)); 3.27 (*t, J* = 2.9, H–C(16)); 5.73 (*s*, H–C(3)); 5.79 (*dt, J* = 1.7, 3.2, H–C(6)). ^{13}C-NMR (100 MHz, $CDCl_3$): 17.9 (*q*, C(18)); 20.9 (*q*, MeCO); 22.7 (*t*, C(14)); 24.1 (*q*, C(17)); 25.8 (*q*, C(20)); 26.5 (*t*, C(10)); 28.3 (*q*, C(19)); 35.1(*t*, C(13)); 35.2 (*d*, C(12)); 36.2 (*t*, C(11)); 40.9 (*t*, C(9)); 41.3 (*t*, C(5)); 54.7 (*s*, C(4)); 59.5 (*d*, C(16)); 73.9 (*s*, C(8)); 76.5 (*d*, C(3)); 128.4 (*d*,

C(6)); 136.7 (*s*, C(1)); 148.1 (*s*, C(7)); 154.7 (*s*, C(15)); 170.9 (*s*, Me*C*O); 193.2 (*s*, C(2)). HR-MS: 360.2306 ($C_{22}H_{32}O_4^+$; calc. 360.2301).

Data of **32**. Colorless gum. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.85 (br. *s*, Me(20)); 1.17 (*s*, Me(18)); 1.28–1.38 (*m*, H–C(9), H–C(13)); 1.48–1.56 (*m*, H–C(5), H–C(13)); 1.65–1.84 (*m*, 2 H–C(6), 2 H–C(10)); 1.94 (*s*, Me(17)); 2.10–2.17 (*m*, H–C(9), H–C(14)); 2.23 (*s*, Ac); 2.45 (*dt*, *J* = 6.8, 13.4, H–C(5)); 2.91 (*dd*, *J* = 5.6, 13.4, H–C(14)); 2.73 (br. *s*, H–C(16)); 5.17 (*s*, H–C(19)); 5.42 (*s*, H–C(19)); 5.75 (*s*, H–C(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): 20.8 (*q*, *Me*CO); 21.2 (*q*, C(18)); 21.9 (*q*, C(20)); 22.0 (*t*, C(14)); 22.7 (*q*, C(17)); 23.8 (*t*, C(10)); 28.2 (*t*, C(9)); 28.4 (*d*, C(12)); 31.1 (*t*, C(13)); 31.7 (*t*, C(11)); 34.4 (*t*, C(6)); 40.0 (*t*, C(5)); 50.3 (*s*, C(4)); 68.3 (*d*, C(16)); 74.1 (*d*, C(3)); 87.8 (*s*, C(7)); 110.5 (*t*, C(19)); 135.4 (*s*, C(1)); 150.1 (*s*, C(8)); 152.3 (*s*, C(15)); 171.0 (*s*, Me*C*O); 193.1 (*s*, C(2)). HR-MS: 360.2289 ($C_{22}H_{32}O_4^+$; calc. 360.2301).

2-Oxotrinervita-1(15)-ene-3α,8α-diol 3α-Acetate (**28a**). A mixture of **30a** (30 mg, 0.083 mmol) and PtO_2 (6.0 mg, 0.026 mmol) in MeOH (1 ml) was vigorously stirred under H_2 for 22 h, and the mixture was filtered through a pad of SiO_2 (3 g) and washed with CH_2Cl_2 (15 ml). The combined org. extract was evaporated, and the residue was purified by CC (hexane/AcOEt 8:1): 29 mg (96%) of **28a**. Colorless needles. M.p. 202–204° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86 (*d*, *J* = 6.1, Me(20)); 0.86–0.95 (*m*, H–C(12)); 1.07 (*s*, Me(18)); 1.12–1.34 (*m*, H–C(5), H–C(9), H–C(10), 2 H–C(11), H–C(13)); 1.18 (*s*, Me(19)); 1.48–1.61 (*m*, H–C(10), H–C(13)); 1.70 (*dddd*, *J* = 6.4, 11.4, 12.8, 13.2, H–C(6)); 1.71 (*dd*, *J* = 6.4, 14.7, H–C(5)); 1.90 (*ddd*, *J* = 7.1, 8.6, 13.2, H–C(6)); 2.15–2.24 (*m*, H–C(9), H–C(14)); 2.18 (*s*, Me(17)); 2.21 (*s*, Ac); 2.61 (*d*, *J* = 11.4, H–C(16)); 2.77 (*dt*, *J* = 8.6, 11.4, H–C(7)); 2.82 (*ddd*, *J* = 4.9, 10.4, 14.7, H–C(14)); 5.75 (*s*, H–C(3)). ^{13}C-NMR (125 MHz, $CDCl_3$): 18.4 (*t*, C(10)); 20.6 (*q*, C(18)); 20.8 (*q*, *Me*CO); 22.17 (*q*, C(20)); 22.22 (*t*, C(14)); 24.8 (*q*, C(17)); 28.2 (*d*, C(12)); 28.5 (*t*, C(6)); 29.1 (*t*, C(9)); 31.2 (*t*, C(13)); 31.6 (*q*, C(19)); 33.3 (*t*, C(11)); 35.8 (*t*, C(5)); 51.5 (*s*, C(4)); 55.7 (*d*, C(7)); 57.5 (*d*, C(16)); 74.1 (*s*, C(8)); 74.4 (*d*, C(3)); 138.3 (*s*, C(1)); 155.4 (*s*, C(15)); 170.9 (*s*, Me*C*O); 193.4 (s, C(2)). HR-MS: 362.2455 ($C_{22}H_{34}O_4^+$; calc. 362.2457).

2-Oxotrinervita-1(15),8(19)-dien-3α-ol Acetate (**27**). Under N_2, $SOCl_2$ (0.012 ml, 0.16 mmol) was added to a stirred mixture of **28a** (29 mg, 0.08 mmol) and pyridine (0.13 ml, 1.61 mmol) in CH_2Cl_2 (1 ml) at 25°, and the mixture was stirred at 25° for 1 h. A sat. aq. $NaHCO_3$ soln. (3 ml) was added, and the mixture was extracted with Et_2O (3 × 10 ml). The combined org. extract was washed with brine (3 × 5 ml), dried (Na_2SO_4) and evaporated, and the residue purified by CC (hexane/AcOEt 15:1): 28 mg (97%) of a white solid. The solid was purified by $AgNO_3$-SiO_2 CC (hexane/AcOEt 100:1 → 60:1): 14.3 mg (52%) of **26**, 9.5 mg (34%) of **27** and 2.9 mg (11%) of 3α-hydroxytrinervita-1(15),8-dien-2-one Acetate **33**.

Data of **27**. Colorless gum. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.84 (*d*, *J* = 5.8, Me(20)); 0.86–1.03 (*m*, H–C(11), H–C(12)); 1.09 (*s*, Me(18)); 1.35 (*ddd*, *J* = 5.1, 7.1, 13.7, H–C(13)); 1.39 (*dd*, *J* = 7.1, 13.2, H–C(5)); 1.48 (*ddt*, *J* = 5.4, 6.8, 13.7, H–C(13)); 1.80 (*dd*, *J* = 6.6, 13.2, H–C(5)); 1.86 (*ddd*, *J* = 7.1, 8.6, 13.9, H–C(6)); 1.96 (*s*, Me(17)); 1.94–2.06 (*m*, H–C(6), 2 H–C(9)); 2.15 (*dt*, *J* = 7.1, 13.7, H–C(14)); 2.22 (*s*, Ac); 2.68 (*dd*, *J* = 6.8, 13.7, H–C(14)); 2.70 (*d*, *J* = 12.0, H–C(16)); 3.40 (*ddd*, *J* = 8.6, 10.7, 12.0, H–C(7)); 4.95 (br. *s*, H–C(19)); 5.03 (br. *s*, H–C(19)); 5.80 (*s*, H–C(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): 20.8 (*q*, *Me*CO); 21.0 (*q*, C(18)); 21.9 (*q*, C(20)); 22.0 (*t*, C(14)); 23.3 (*q*, C(17)); 23.7 (*t*, C(10)); 27.2 (*t*, C(9)); 28.2 (*d*, C(12)); 29.4 (*t*, C(6)); 31.2 (*t*, C(13)); 32.0 (*t*, C(11)); 36.8 (*t*, C(5)); 49.8 (*s*, C(4)); 52.5 (*d*, C(7)); 58.7 (*d*, C(16)); 74.8 (*d*, C(3)); 113.9 (*t*, C(19)); 135.2 (*s*, C(1)); 149.6 (*s*, C(8)); 151.9 (*s*, C(15)); 170.9 (*s*, Me*C*O); 193.5 (*s*, C(2)). HR-MS: 344.2357 ($C_{22}H_{32}O_3^+$; calc. 344.2351).

Data of **33**. Colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86 (*d*, *J* = 6.8, Me(20)); 1.10 (*s*, Me(18)); 1.76 (*s*, Me(19)); 2.22 (*s*, Me(17)); 2.23 (*s*, Ac); 2.63 (*d*, *J* = 11.0, H–C(16)); 3.08 (*td*, *J* = 9.2, 11.0, H–C(7)); 5.37 (*dd*, *J* = 3.7, 9.5, H–C(9)); 5.62 (*s*, H–C(3)). ^{13}C-NMR (125 MHz, $CDCl_3$): 20.7 (*q*); 21.1 (*q*); 21.6 (*q*); 21.7 (*q*); 22.2 (*t*); 22.4 (*q*); 24.6 (*t*); 28.4 (*d*); 32.4 (*t*); 32.8 (*t*); 34.3 (*t*); 36.6 (*t*); 49.5 (*s*); 50.2 (*d*); 60.6 (*d*); 75.1 (*d*); 128.7 (*d*); 134.6 (*s*); 135.8 (*s*); 153.2 (*s*); 170.8(*s*); 193.5 (*s*).

Trinervita-1(15),8(19)-diene-2α,3α-diol (**2b**) *and Trinervita-1(15),8(19)-diene-2β,3α-diol* (**2a**). $LiAlH_4$ (3.0 mg, 0.08 mmol) was added to a soln. of **27** (9.5 mg, 0.028 mmol) in THF (0.5 ml) at −20°, and the mixture was stirred at −20° for 1 h. Then MeOH (0.5 ml) and H_2O (5 ml) were added, and the mixture was extracted with Et_2O (3 × 15 ml), and the org. phase was washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated. The residue purified by CC (hexane/AcOEt 5:1): 4.7 mg (56%) of **2b** and 3.7 mg (44%) of **2a**.

Data of **2b**. Colorless prisms. M.p. 70–72° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.89 (*d*, *J* = 6.7, Me(20)); 1.10 (*s*, Me(18)); 1.78 (*s*, Me(17)); 2.53 (*d*, *J* = 12.2, H–C(16)); 3.24 (*dt*, *J* = 12.2, 9.3, H–C(7)); 3.91 (*d*, *J* = 5.2, 9.0, H–C(3)); 4.07 (*dd*, *J* = 5.2, 5.8, H–C(2)); 4.83 (*m*, H–C(19)); 4.94 (*m*, H–C(19)). ^{13}C-NMR (125 MHz, $CDCl_3$): 22.02 (*q*, C(18)); 22.05 (*q*, C(17)); 22.4 (*q*, C(20)); 24.0 (*t*, C(14)); 26.1 (*t*, C(10)); 27.3 (*t*, C(9)); 27.5 (*d*, C(12)); 29.1 (*t*, C(6)); 32.0 (*t*, C(13)); 32.3 (*t*, C(11)); 37.8 (*t*, C(5)); 45.5 (*s*, C(4)); 52.6 (*d*, C(7)); 58.5 (*d*, C(16));

69.3 (*d*, C(3)); 71.2 (*d*, C(2)); 112.5 (*t*, C(19)); 131.6 (*s*, C(1)); 133.4 (*s*, C(15)); 151.1 (*s*, C(8)). HR-MS: 304.2392 ($C_{20}H_{32}O_2^+$; calc. 304.2402).

Data of **2a**. Colorless prisms. M.p. 169–171° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.92 (*d*, *J* = 6.7, Me(20)); 1.00 (*s*, Me(18)); 1.06–1.13 (*m*, H–C(13)); 1.15–1.26 (*m*, H–C(5), 2 H–C(11)); 1.46–1.54 (*m*, H–C(10)); 1.64-1.85 (*m*, 2 H–C(6), H–C(9), H–C(10), H–C(12), H–C(13)); 1.74 (*d, J* = 1.9, Me(17)); 2.04 (*dd, J* = 6.4, 12.8, H–C(5)); 2.12 (*ddd, J* = 4.0, 10.1, 15.3, H–C(9)); 2.20–2.29 (*m*, 2 H–C(14)); 2.39 (*d, J* = 11.6, H–C(16)); 3.16 (*dt, J* = 7.9, 11.6, H–C(7)); 3.83 (*d, J* = 8.9, H–C(3)); 3.96 (br. *d, J* = 8.9 Hz, H–C(2)); 4.77 (*m*, H–C(19)); 4.93 (*m*, H–C(19)). ^{13}C-NMR (125 MHz, $CDCl_3$): 20.4 (*q*, C(18)); 21.8 (*q*, C(17)); 22.6 (*q*, C(20)); 24.3 (*t*, C(14)); 25.1 (*t*, C(10)); 27.2 (*t*, C(9)); 27.6 (*d*, C(12)); 29.7 (*t*, C(6)); 32.3 (*t*, C(13)); 34.6 (*t*, C(11)); 36.5 (*t,* C(5)); 46.3 (*s,* C(4)); 53.1 (*d*, C(7)); 58.1 (*d*, C(16)); 73.1 (*d*, C(3)); 73.7 (*d*, C(2)); 112.0 (*t,* C(19)); 130.0 (*s,* C(1)); 132.1 (*s,* C(15)); 153.0 (*s,* C(8)). HR-MS: 304.2395 ($C_{20}H_{32}O_2^+$; calc. 304.2402).

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