Synthesis of (±)-Kempa-6,8-dien-3-ol (= (2a*RS*,3*SR*,4a*SR*,7*RS*,7a*SR*,10b*SR*,10c*SR*)-2,2a,3,4,4a,5,6,7,7a,8,10b,10c-Dodecahydro-2a,7,10,10c-tetramethylnaphth[2,18-*cde*]azulen-3-ol)[1])

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The synthesis of kempa-6,8-dien-3β-ol (**4a**), as a synthetic leading model of the natural product **4b**, was carried out starting from intermediate **12**, the synthetic route of which has been developed previously (*Scheme 1*). The conversion of **12** to the model compound **4a** involved the elaboration of three structure modifications by three processes, *Tasks A*, *B*, and *C* (see *Scheme 2*). *Task A* was achieved by epoxy-ring opening of **41** with Me_3SiCl (*Scheme 9*), and *Task B* being performed by oxidation at the 13-position, followed by hydrogenation, and then epimerization (*Schemes 4* and *5*). The removal of the 2-OH group from **12** (*Task C*) was achieved *via* **30b** according to *Scheme 6*, whereby **30b** was formed exclusively from **30a**/**31a** 1:1 (*Scheme 7*). In addition, some useful reactions from the synthetic viewpoint were developed during the course of the present experiments.

Introduction. – Several species of termites are known to secrete a variety of biogenetically related cyclic diterpenes. These are monocyclic neocembrene (**1**) as a trail pheromone of termite workers, and bicyclic 7,16-secotrinervitatriene-2,3-diol 2-acetate **2**, tricyclic trinervitadiene-2,3-diol **3**, and tetracyclic 14-acetoxykempa-6,8-dien-3-one **4b** as the defensive substances of termite soldiers (*Fig.*).

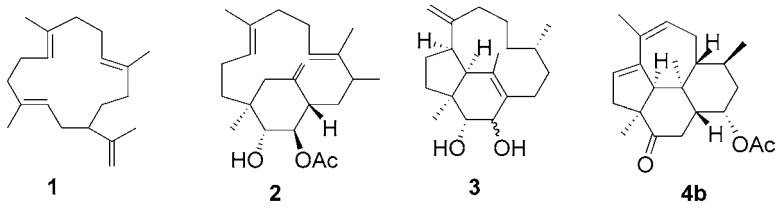


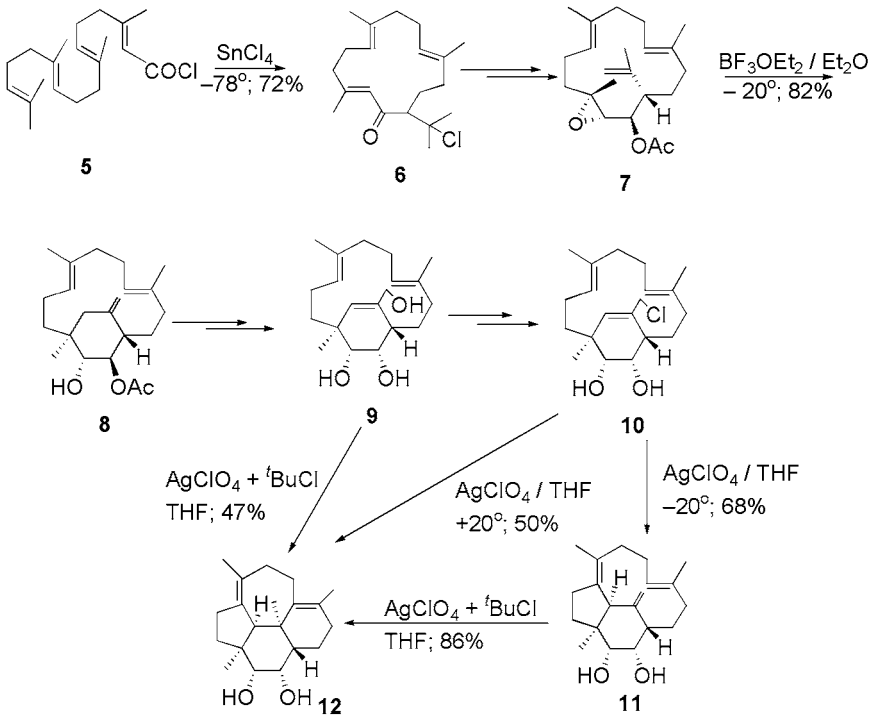
Fig. 1. *Typical diterpenes characterized from termites*

We have been very interested in the synthesis of these biologically and skeletally attracting diterpenoids. The synthetic strategy associated with our exploration of these natural products has been based on the scaffolding power of biogenetic considerations, and we have exploited and accumulated the construction routes starting from geranylgeranic acid chloride **5** as described in the previous paper (*Scheme 1*) [2]. After efficient construction of the cembrene skeleton **6** from acyclic acid chloride **5**, the second cyclization from epoxy acetate **7**, which was easily obtained from the chloro

[1]) Part 63 of the series Cyclization of Polyenes; for Part 62, see [1].

ketone **6**, was achieved to make the natural product 7,16-secotrinervitatriene-2,3-diol 2-acetate **8** (=**2**). The allyl chloride **10**, derived from **8** by subsequent reactions, is a prominent intermediate for the stereoselective third cyclization yielding the skeletons of both trinervitane **11** and kempane **12**. For the practical preparation, the allyl alcohol **9** was directly converted to the kempane skeleton **12**. Further study has been continued to synthesize the biologically intriguing trinervitane- and kempane-type natural products [3]. We now describe the preparation of 14-deacetoxykempa-6,8-dien-3-ol **4a** from the intermediate **12** as a preceding experiment of the synthesis of natural product **4b** (for isolation, see [4]; for synthesis, see [5]).

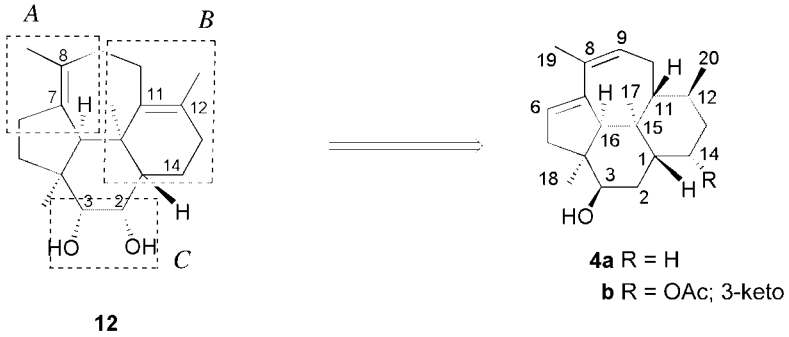
Scheme 1. *Construction of Trinervitane* **11** *and Kempane* **12** *Skeletons*



Results and Discussion. – Elaboration of our intermediate **12** to the kempane-type natural product **4b** needs three major transformation processes (*Scheme 2*), *i.e.*, the selective conversion of the C=C bond at the 7-position to the conjugated diene moiety (*Task A*), the hydrogenation of the tetrasubstituted C(11)=C(12) bond in a *trans*-fashion and introduction of the acetyloxy group at the 14-position (*Task B*), and selective removal of the 2-OH group (*Task C*)[2]).

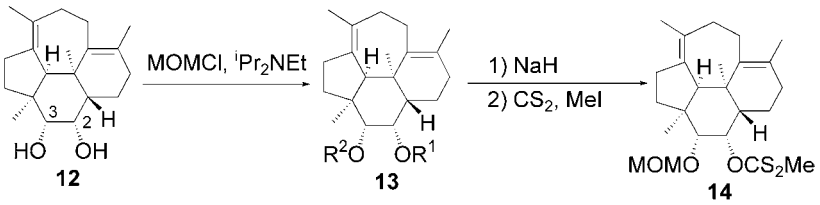
[2]) Trivial numbering; for systematic names, see *Exper. Part*.

Scheme 2. *Transformation of* **12** *to Kempa-6,8-dien-3-ol* **4a**[2])



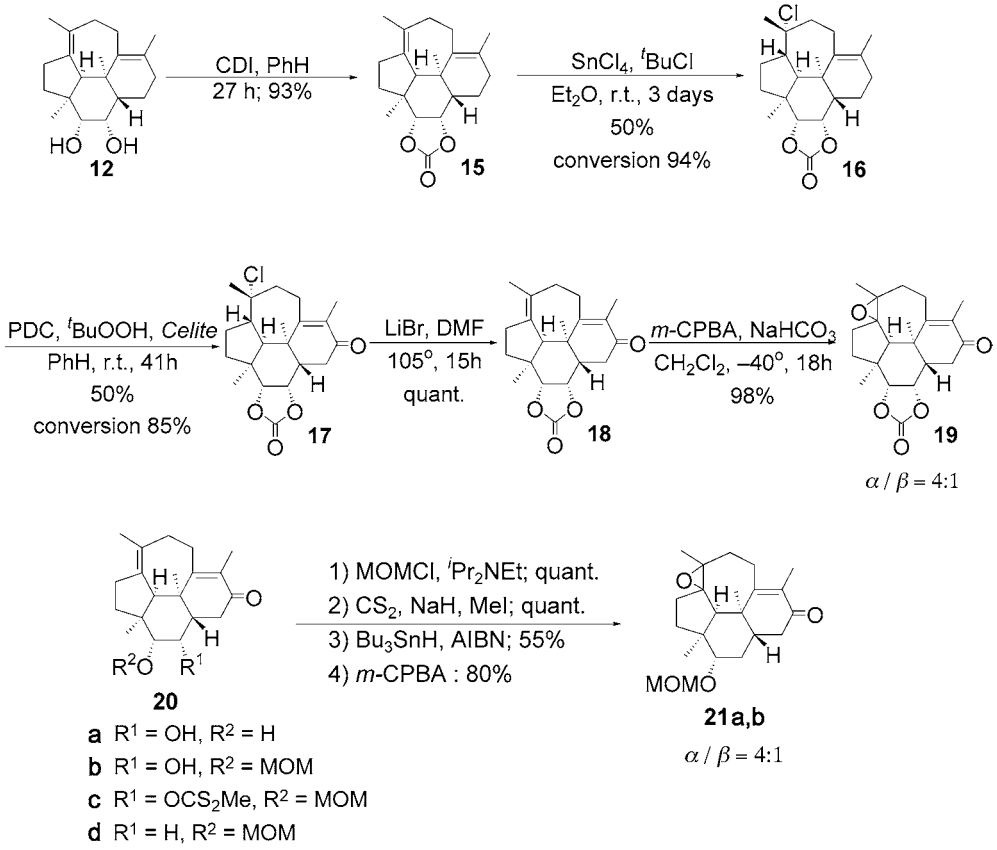
To gain insight into the reactivity of the 2,3-diol part of **12**, we first examined the ether formation reaction with MOMCl (= $MeOCH_2Cl$) (*Scheme 3*). Our preliminary exploratory experiments revealed that the reactivities of the two OH groups are clearly different, and 3-MOM ehter **13a** was the sole product, without formation of bis-MOM ether **13b**, when excess amounts of MOMCl and $^{i}Pr_2NEt$ were applied under the usual conditions. The etherification at the 3-position of **13a** was confirmed by the coupling mode of H–C(2) (δ(H) 6.36 (*dd*, $J = 1.5$, 3.7 Hz)) of the methyl carbonodithioate **14** derived therefrom. The selective protection of the 3-OH group seemed highly encouraging for the removal of the 2-OH group. However, for the ongoing protection of the 2,3-diol part, the carbonate was the better choice owing to the efficient formation [6] of carbonate **15** from **12** (*Scheme 4*). On achievement of *Task B* (see *Scheme 2*), the dienone **18** was set up as the key intermediate to distinguish the two C=C bonds in **12** for selective hydrogenation of the C(11)=C(12) bond. The carbonyl function adjacent to the latter C=C bond may help the introduction of the H-atoms in the *trans*-fashion. Selective epoxidation of the isolated C(7)=C(8) bond of **18** is required for its protection prior to hydrogenation, and the generated epoxy ring may serve for the conjugated diene formation (*Task A*).

Scheme 3. *Reactivity of the 2,3-Diol Moiety of* **12**



As anticipated, the trials to obtain the conjugated enone **18** by direct allylic oxidation of **15** with pyridinium chlorochromate (PCC) or pyridinium dichromate (PDC) under the usual conditions gave no satisfactory results, leading to a product mixture containing **18** in low yield (28%). Thus, the C(7)=C(8) bond of **15** had to be

Scheme 4. *Preparation of Epoxyenone* **19**



CDI = 1,1′-carbonylbis[1*H*-imidazole], PDC = pyridinium dichromate, *m*-CPBA = 3-chloroperbenzoic acid, MOMCl = $MeOCH_2Cl$, AIBN = 2,2′-azobis[2-methylpropanenitrile]

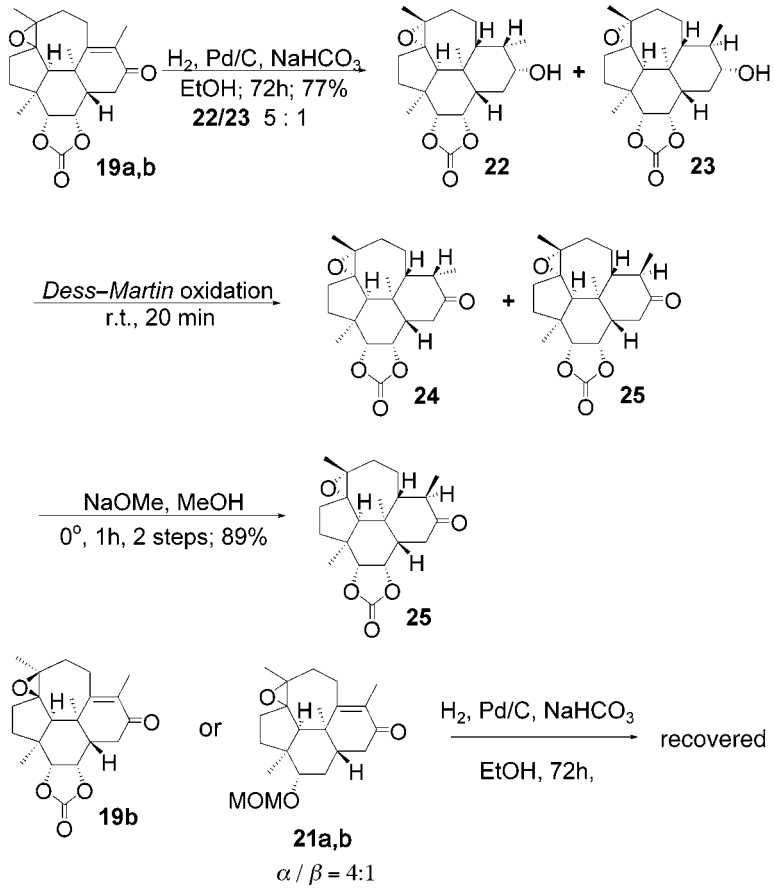
protected first. Oxidation with 3-chloroperbenzolic acid (*m*-CPBA) at low temperature gave a mixture of the predominant 7,8-epoxy and the minor 11,12-epoxy derivative, respectively, suggesting that the C(7)=C(8) bond is more reactive as compared with the C(11)=C(12) bond. Fortunately, the position-selective addition of HCl with bulky $HSnCl_5$, prepared *in situ* from $SnCl_4$ and ^{t}BuCl in Et_2O, took place efficiently, affording a mixture of chloro derivative **16** and recovered **15** (*Scheme 4*). After separation and recycling of **15**, **16** was accumulated in 94% conversion yield. When CH_2Cl_2 was employed instead of Et_2O as the solvent, no selectivity for the position of HCl addition was observed at all. The positions and configurations of the newly introduced H- and Cl-atoms were established by detailed comparison of the ^{1}H-NMR spectra of **16** and **15** [7] (**16**: NOE of H–C(7) at δ(H) 1.77 (*m*) with both Me–C(8) at δ(H) 1.53 (*s*) and H–C(1) at δ(H) 1.56 (*m*)). The allylic oxidation at C(13) of **16** proceeded smoothly by the action of PDC and ^{t}BuOOH in the presence of *Celite* [8] to give the enone **17** in 85% conversion yield. Dehydrochlorination of **17** under the usual conditions provided

the tetrasubstituted dienone **18** in quantitative yield, no C=C bond isomer being detected in this reaction. A low-temperature *m*-CPBA oxidation of **18** in the presence of $NaHCO_3$ afforded exclusively a 4:1 stereoisomer mixture of 7,8-epoxy derivatives **19**, the α-epoxy isomer being predominant; the lesser amount of β-isomer may be a consequence of the congested nature of the β-face as suggested by *Dreiding* models. Several attempts to increase the selectivity for the α-epoxy isomer were unsuccessful, *i.e.*, epoxidation of **18** with magnesium monoperoxyphthalate hexahydrate (MMPP) [9] resulted in a decrease of the α/β ratio to 3:2. Although the α/β ratio of the 7,8-epoxy derivatives increased to 6:1 when *m*-CPBA was applied to the model compound **13a** (*Scheme 3*), selective deprotection of the MOM group was unsuccessful under various acidic conditions due to the more-labile nature of the epoxy ring of the product. As alternative candidates for synthetic intermediates, a 4:1 mixture of the epoxyenone **21a**/**21b** was prepared *via* the position-selective MOM-ether formation of **20a**, which was easily derived from **18** (*Scheme 4*).

The selective reactivity of the C(11)=C(12) bond was examined with the enones **17**–**19**. The reaction of **18** with metal (Li, Na) under *Birch* conditions [10] resulted in the formation of a complex mixture or recovery of the starting material. Treatment of **18** with $NaBH_4$/pyridine [11] or $LiAlH_4$/CuI [12] afforded the corresponding allyl alcohol, without reduction of the C(11)=C(12) bond but with deprotection of the carbonate group. The application of Mg in MeOH [13] to **18** was also unsuccessful. Hydrogenation of **17** in MeOH in the presence of PtO_2 led to the exclusive formation of the 13α-allyl alcohol after 15 min. Extension of the reaction time to 2 h under the same conditions resulted in the replacement of the Cl-atom at C(8) with a H-atom without reduction of the C(11)=C(12) bond. Attempts of the hydrogenation of **18** were also unsuccessful; the 7,11-dien-13α-ol was the sole product when H_2 was applied in the presence of PtO_2 in MeOH.

Hydrogenation in the presence of 5% Pd/C was different from that of PtO_2, *i.e.*, the reaction of epoxyenones **19a**/**19b** with H_2 in the presence of 5% Pd/C and $NaHCO_3$ afforded a 5:1 mixture of alcohols **22** and **23** in 77% yield, accompanied by the recovered β-epoxyenone **19b** in 20% yield, easily separated from the alcohols by column chromatography (silica gel) (*Scheme 5*). After careful separation of **22** and **23**, each was submitted to the *Dess–Martin* reagent to give **24** from **22** and **25** from **23**, respectively. Ketone **24** was easily and quantitatively converted to **25** by the action of NaOMe/MeOH at 0° for 1 h. The exclusive formation of reduction products with a β-positioned H–C(11) indicates that entry of the H-atom proceeded from the sterically less-congested π-surface of **19a**. The minor alcohol **23** may be formed by 1,4-H addition to the conjugated enone moiety, followed by protonation at C(12) from the α-face and subsequent hydrogenation of the resulting carbonyl group from the β-face. The configuration of **23** was confirmed by the reduction of **25** with $NaBH_4$, which gave exclusively the same alcohol **23**. The inertia of **19b** toward reaction under the hydrogenation conditions is attributed to the crowded π-surface of the C(11)=C(12) bond due to the β-epoxy moiety. In the practical preparation of ketone **25**, the crude alcohol mixture **22**/**23** was, after separation of **19b**, successively treated with *Dess–Martin* reagent and NaOMe, providing the target ketone **25** in 89% overall yield from the hydrogenated products. The trials to recycle the recovered **19b** to **18** were unsuccessful with SmI_2 [14] or $(C_6H_5)_3P$ in the presence of I_2 [15] or HI [16]. It is

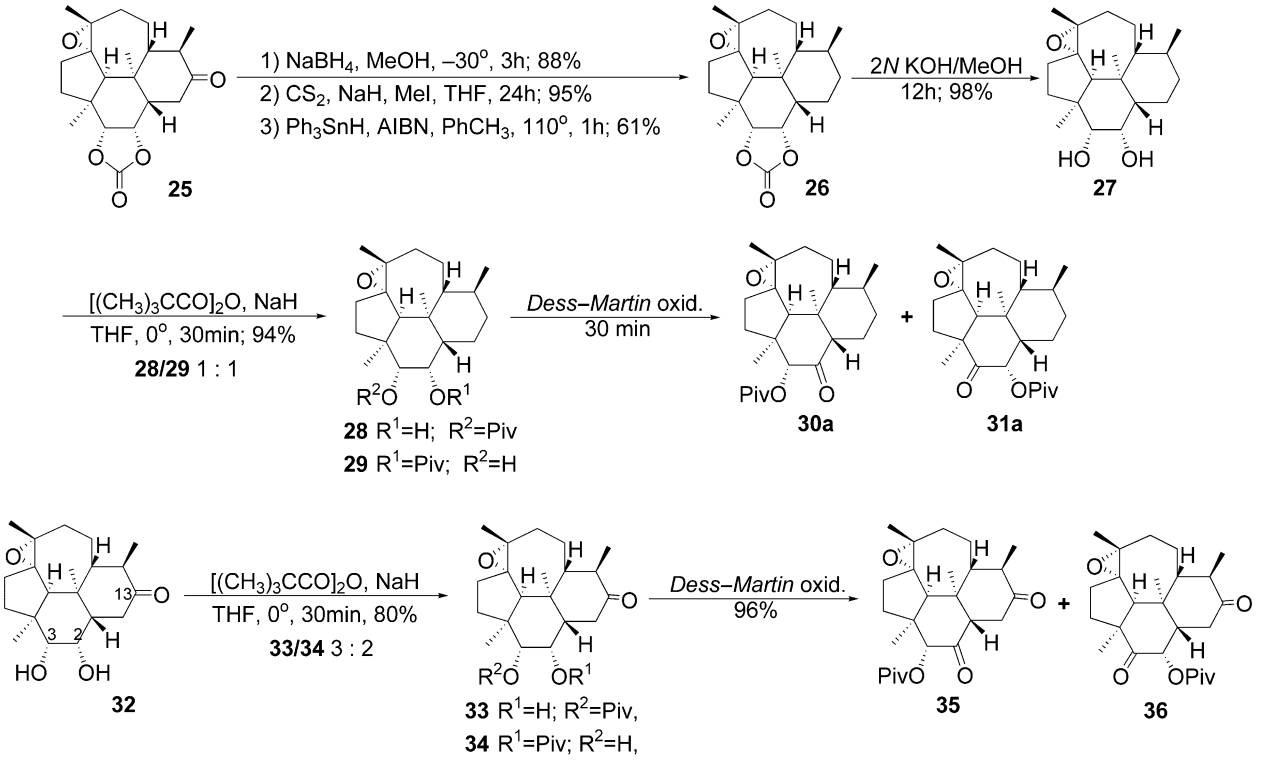
Scheme 5. *Hydrogenation of the 11,12-Double Bond*



worthy of comment that the 3-MOMO-epoxyenone mixture **21a**/**21b** is inert under the hydrogenation conditions, indicating that the carbonate moiety at the 2,3-position of **19** affects the conformation of the whole molecule to that suitable for hydrogenation. In fact, the ^{1}H-NMR coupling modes of H–C(2) of **18** and of the corresponding diol derivative **20c** are fairly different (**18**: $J(1,2) = 4.6$ Hz and $J(2,3) = 9.3$ Hz; **20c**: $J(1,2) = 2.4$ Hz and $J(2,3) = 3.4$ Hz).

The removal of the O-atom from the 13-position was an easy task; reduction of **25** with $NaBH_4$ provided preferentially the 13α-hydroxy epoxide **23**, identical to the minor product obtained by hydrogenation of **19** (*Scheme 5*). The OH group was removed by methyl carbonodithioate formation, followed by reductive removal of the carbonodithioate group through a radical process, affording the desired deoxygenated product **26** (*Scheme 6*). Hydrolysis of the protecting carbonate ring under alkaline conditions furnished the epoxydiol **27**.

Scheme 6. *Preparation of Keto Pivalates*



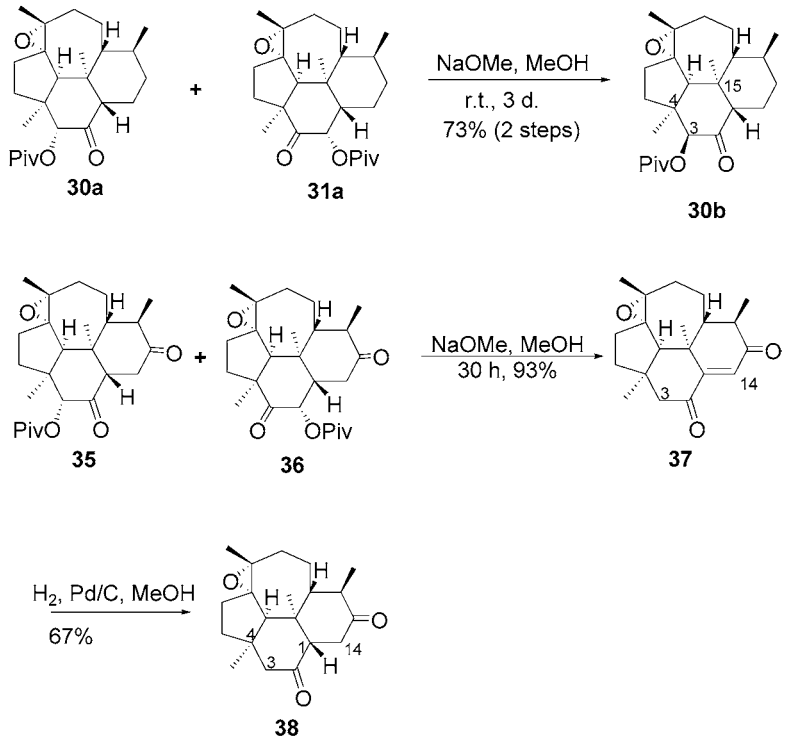
Contrary to expectations, the selective protection of the 3-OH group was found to be difficult by means of MOM, ^{t}BuMe$_2$Si, or pivalate group, all of which provided a *ca.* 1:1 mixture of derivatives mono-protected at the 2- and 3-positions. The reaction of diol **27** with excess amounts of pivalic anhydride in the presence of NaH resulted in the formation of a 1:1 mixture of monopivalates **28** and **29**, which were converted to the corresponding keto pivalates **30a** and **31a** (1:1). Separation of the mixtures **28**/**29** or **30a**/**31a** was difficult by the usual chromatography, and, hence, the protection of the 2,3-diol moiety of **32**, prepared from **25** by alkaline hydrolysis, was also examined. As in the case of **27**, almost no selective reactivity of the two OH groups of **32** was observed, affording a 3:2 mixture of monopivalates **33** and **34**. It should be noted that the reactivity of the 2,3-diol moiety of kempa-7,11-diene derivatives **13** and **20a** was completely different, the 3-OH group being selectively protected.

Since the selective protection of the 3-OH group of the 2,3-diols **27** and **32** gave unsuccessful results, an equilibrium-controlled isomerization of keto pivalates through the enolate intermediates was next attempted. It might be expected that, under strongly basic conditions, the most-stable isomer would be exclusively formed from both isomers of keto pivalates **30a** and **31a** *via* the common orthoester-type intermediate **A**, thermodynamics playing the key role in determining the direction (see below, *Scheme 8*). Assuming that the cyclohexanone ring of **30** and **31** is in a boat conformation (*Dreiding* model), the 3α-OPiv compound **30a** is sterically more crowded than the corresponding 3β-OPiv derivative **30b** due to the steric congestion between the OPiv group and Me–C(4) and Me–C(15). Our preliminary MM2 calculation of the pairs of **30a**,**b** and **31a**,**b** suggests the following order of the molecular energies: **30b** (3β-OPiv) < **30a** < **31b** (2β-OPiv) < **31a**. Based on the considerations described so far, we tried the enolization of **30a** and **31a** with NaOMe/MeOH at room temperature. Under these conditions, the 1:1 mixture **30a**/**31a** was transformed to the single product **30b** in a 73% yield (*Scheme 7*). The structure of **30b** was confirmed by its NMR spectra (NOE of H$_\alpha$–C(3) (δ(H) 5.42 (*s*)) with Me$_\alpha$–C(4) and Me$_\alpha$–C(15)). When 13-keto derivatives **35** and **36**, obtained easily from monopivalates **33** and **34** (*Scheme 6*), were submitted to the similar treatment with NaOMe/MeOH, an unexpected product was formed, *i.e.*, treatment of isolated **35** resulted in the formation of the epoxyenedione **37** in 93% yield (*Scheme 7*); isomer **36** afforded the same compound **37** in the same yield. The structure of **37** was confirmed by a detailed analysis of the NMR spectra of its dihydro derivative **38**, demonstrating the presence of H-atoms at C(14), C(1), and C(3) as shown by the assigned structure. The plausible conversion mechanism for **30a**/**31a** → **30b** *via* **A** and **B** and for **35** or **36** → **37** *via* **A**′ and **C** is documented in *Scheme 8* where the initial formation of orthoester intermediates **A** and **A**′ may play the central role in the observed transformations.

Removal of the 2-oxo group from keto pivalate **30b** proceeded smoothly *via* the methyl carbonodithioate intermediate **40**, which, in turn, was prepared from 2β-hydroxy derivative **39** (*Scheme 9*). The 2β-configuration of **39**, predominantly derived from **30b** by the reduction with NaBH$_4$, was supported by NOESY experiments (clear cross-peak H$_\alpha$–C(2)/Me$_\alpha$–C(4)). The quantitative conversion of **40** to **41** was achieved by treatment with Ph$_3$SnH in the presence of AIBN.

The attention shifted finally to the transformation of the epoxy group to the diene moiety. This objective was met efficaciously by treatment of **41** with Me$_3$SiCl in THF at

Scheme 7. *Reaction of Keto Pivalates with NaOME*



room temperature, furnishing the kempa-6,8-diene derivative **42** in quantitative yield[3]) (*Scheme 9*). The structure of **42** and **4a** (obtained after $LiAlH_4$ treatment) was supported by the ^{1}H-NMR spectra, the corresponding signals of the major protons being compared with those of the reported values [4a] of the natural product **4b** (*Table*). The ^{13}C-NMR spectra clearly confirmed the assigned structure of **4a**.

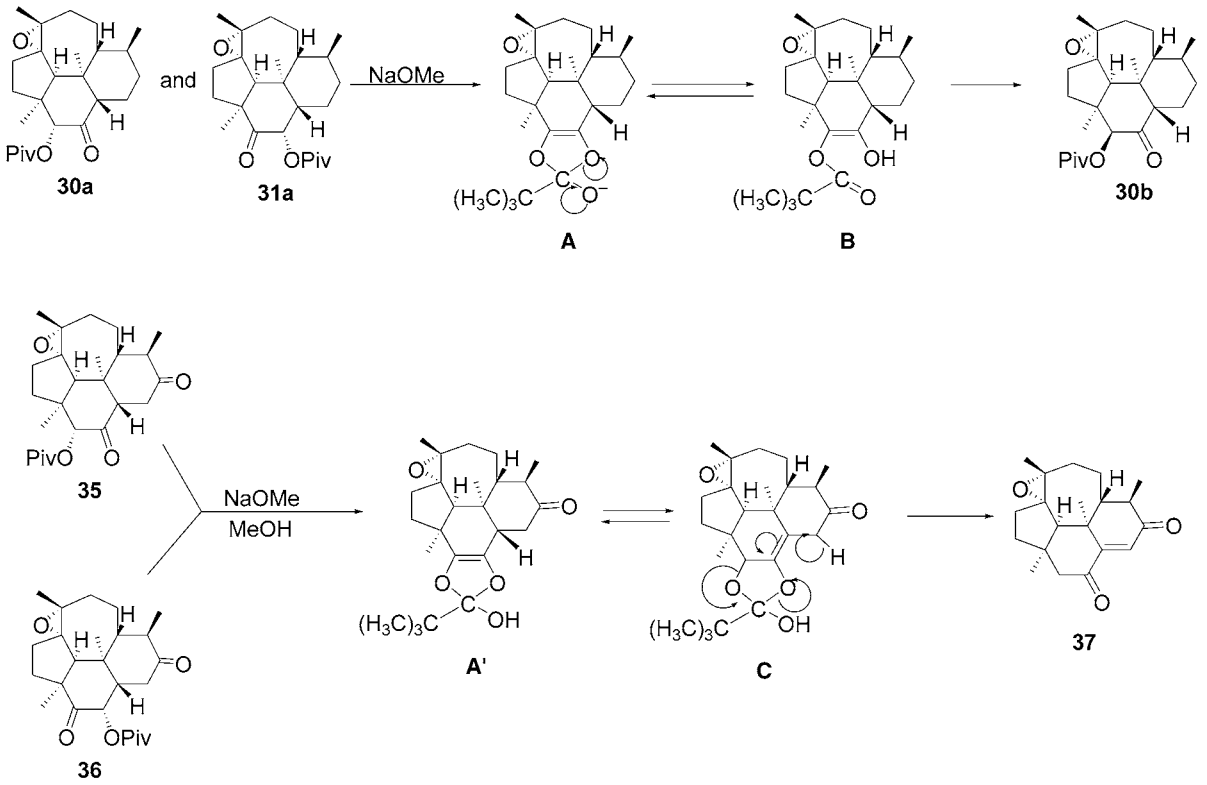
Thus, the conversion route of the kempane skeleton **12** to the kempa-6,8-dien-3-ol was developed in the present study in which, additionally, some useful reactions from the synthetic viewpoint were disclosed. By means of the accumulated evidence described so far, the synthesis of **4b** and other kempane-type natural products is expected to be achieved and is now in progress.

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) and Et_2O were distilled from sodium benzophenone radical ion (1 –), and hexane was distilled from P_2O_5 for the respective reaction solvents. Distilled Et_2O and AcOEt were used for extraction. Anal. TLC: aluminium sheets coated with silica gel *60 F_{254}*, hexane/AcOEt mixtures; visualization with UV light and then staining with 0.5% anisaldehyde in 2M aq. H_2SO_4

[3]) Successful application of Me_3SiCl for the epoxide-ring-opening reaction was also performed in our trinervitane synthesis [3].

Scheme 8. *Mechanism of Conversion of Keto Pivalates by NaOMe*



Scheme 9. *Derivation to Kempa-6,8-dien-3-ol* **4a**

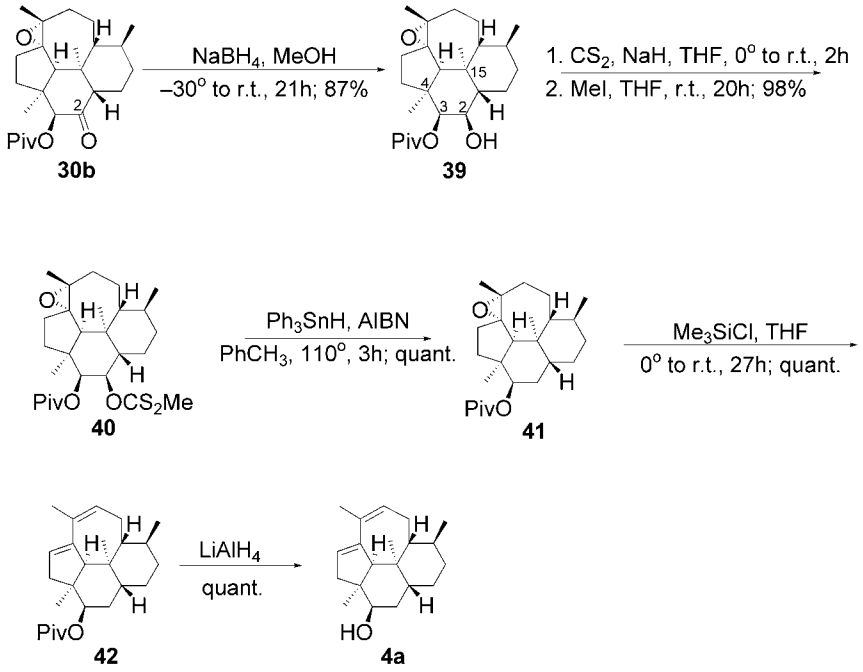


Table. *^{1}H-NMR Spectra* ($CDCl_3$) *of Synthetic 3-Pivalate* **42** *and Natural 3-Keto 14-Acetate* **4b**. δ in ppm, J in Hz[a])

	δ(H)	
	4b	**42**
H–C(3)		5.13 (*dd*, J = 7.6, 9.2)
H–C(5)	2.30 (br. *d*, J = 16.0)	1.92 (*dd*, J = 3.4, 17.4)
H–C(5)	2.72 (br. *d*, J = 16.0)	2.73 (*d*, J = 17.4)
H–C(6)	5.70 (br. *s*)	5.62 (br. *s*)
H–C(9)	5.76	5.68 (br. *d*, J = 7.6)
H–C(16)	2.35 (*d*, J = 2.0)	2.26 (*d*, J = 1.9)
Me(17)	0.94 (*s*)	0.91 (*s*)
Me(18)	1.14 (*s*)	1.00 (*s*)
Me(19)	1.85 (*d*, J = 1.5)	1.82 (*s*)
Me(20)	0.88 (*d*, J = 6.0)	0.81 (*d*, J = 6.4)
Me_3CCO		1.20 (*s*)

[a]) **4b** at 220 MHz and **42** at 500 MHz.

soln. CC (column chromatography): silica gel *Merck 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: $CDCl_3$ soln. with $SiMe_4$ as internal standard, *Jeol* spectrometers; δ in ppm, J in Hz; assignments based on reference compound **12**; the purity of all the compounds was confirmed by ^{13}C-NMR; trivial numbering[2]) (see *Scheme 2*). MS: *Hitachi M-80B* spectrometer. Combustion analyses: *Yanaco MT-6* CHN recorder.

3α-(Methoxymethoxy)kempa-7,11-dien-2α-ol (=*(2a*RS,*3*SR,*4*RS,*4a*RS,*10b*RS,*10c*SR*)-1,2,2a,3,4,4a,5,6,8,9,10b,10c-Dodecahydro-3-(methoxymethoxy)-2a,7,10,10c-tetramethylnaphth[2,1,8*-cde*]azulen-4-ol*; **13a**). Under N_2, a mixture of **12** (21 mg, 0.069 mmol), $^iPr_2NEt$ (72 µl, 0.42 mmol), and $MeOCH_2Cl$ (26 µl, 0.35 mmol) in CH_2Cl_2 (2 ml) was stirred at 20° for 23 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 × 10 ml), the combined org. phase washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaprated, and the residue purified by CC (hexane/AcOEt 15:1): 19 mg (79%) of **13a**. White powder (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.34 (*s*, Me); 1.37 (*s*, Me); 1.51 (*s*, Me); 1.57 (*s*, Me); 2.90 (br. *s*, H−C(16)); 3.37 (*d*, *J* = 3.7, H−C(3)); 3.45 (*s*, MeO); 3.96 (*dd*, *J* = 2.2, 3.7, H−C(2)); 4.68, 4.80 (2*d*, each *J* = 6.7, MeOC*H*$_2$O). HR-MS: 346.2516 ($C_{22}H_{34}O_3^+$; calc. 346.2508). Anal. calc. for $C_{22}H_{34}O_3$: C 76.26, H 9.89; found: C 76.50, H 9.45.

3α-(Methoxymethoxy)-2α-[(methylthio)thioxomethoxy]kempa-7,11-diene (=O-*[(2a*RS,*3*SR,*4*RS,*4a*RS,*10b*RS,*10*SR*)-1,2,2a,3,4,4a,5,6,8,9,10b,10c-Dodecahydro-3-(methoxymethoxy)-2a,7,10,10c-tetramethylnaphth-[2,1,8*-cde*]azulen-4-yl]* S-*Methyl Carbonodithioate*; **14**). Under N_2, CS_2 (100 µl) and MeI (100 µl) were successively added to a stirred mixture of **13a** (19 mg, 0.055 mmol) and NaH (50 mg, excess) in THF (5 ml) at 20°. After stirring for 4 h, sat. aq. NH_4Cl soln. (5 ml) and H_2O (5 ml) were added. The mixture was extracted with Et_2O (3 × 10 ml), the combined org. phase washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 40:1): 24 mg (quant.) of **14**. Oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.30 (*s*, Me); 1.38 (*s*, Me); 1.53 (*s*, Me); 1.55 (*s*, Me); 2.59 (*s*, CS_2Me); 2.98 (br. *s*, H−C(16)); 3.41 (*s*, MeO); 3.61 (*d*, *J* = 3.7, H−C(3)); 4.44, 4.88 (2*d*, each *J* = 7.4, MeOC*H*$_2$O); 6.36 (*dd*, *J* = 1.5, 3.7, H−C(2)). HR-MS: 436.2128 ($C_{24}H_{36}O_3S_2^+$; calc. 436.2106).

Kempa-7,11-diene-2,3-diol 2,3-Carbonate (=*(2a*RS,*3*SR,*4*RS,*4a*RS,*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 Carbonate*; **15**). Under N_2, a mixture of **12** (408 mg, 1.35 mmol) and 1,1′-carbonylbis[1*H*-imidazole] (667 mg, 4.10 mmol) in benzene (12 ml) was stirred at 20° for 27 h. After dilution with H_2O (10 ml), the mixture was extracted with AcOEt (3 × 7 ml), the combined org. phase washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 5:1): 414 mg (93%) of **15**. Colorless needles. M.p. 181–183° (hexane). IR (CCl_4): 2936, 1812, 1744, 1454, 1378, 1182, 1068. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.88 (*dd*, *J* = 4.6, 9.5, H−C(2)); 4.70 (*d*, *J* = 9.2, H−C(3)); 2.70 (br. *s*, H−C(16)); 1.58 (*s*, Me); 1.55 (*s*, Me); 1.24 (*s*, Me); 1.12 (*s*, Me). ^{13}C-NMR (125 MHz, $CDCl_3$): 155.0 (*s*); 136.4 (*s*); 135.2 (*s*); 128.8 (*s*); 124.5 (*s*); 80.0 (*d*); 78.6 (*d*); 54.1 (*d*); 44.9 (*s*); 41.7 (*s*); 38.1 (*t*); 36.5 (*t*); 36.4 (*d*); 31.2 (*t*); 28.9 (*t*); 26.9 (*q*); 23.7 (*t*); 22.3 (*q*); 22.2 (*q*); 20.8 (*t*); 18.9 (*q*). HR-MS: 328.2047 ($C_{21}H_{28}O_3^+$; calc. 328.2038). Anal. calc. for $C_{21}H_{28}O_3$: C 76.79, H 8.59; found: C 76.50, H 8.45.

8-Chlorokemp-11-ene-2,3-diol 2,3-Carbonate (=*(2a*RS,*3*SR,*4*RS,*4a*RS,*10b*RS,*10c*SR*)-10-Chloro-1,2,2a,3,4,4a,5,6,8,9,10,10a,10b,10c-tetradecahydro-2a,7,10,10c-tetramethylnaphth[2,1,8*-cde*]azulene-3,4-diol Carbonate*; **16**). Under N_2, ^{t}BuCl (1.3 ml, 13.5 mmol) and $SnCl_4$ (1.1 ml, 8.98 mmol) were successively added to an Et_2O (50 ml) soln. of **15** (295 mg, 898 µmol), and the mixture was stirred at 20° for 3 days. The mixture was poured into sat. aq. $NaHCO_3$ soln. (30 ml), the aq. phase extracted with AcOEt (2 × 10 ml), the combined org. phase washed successively with sat. aq. $NaHCO_3$ soln. (3 × 30 ml) and brine (3 × 30 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 5:1): 163 mg (50%) of **16** and 139 mg (47%) of recovered **15**. **16**: Colorless needles. M.p. 181–183° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 4.89 (*dd*, *J* = 4.9, 9.5, H−C(2)); 4.67 (*d*, *J* = 9.5, H−C(3)); 2.25 (*m*, H−C(16)); 2.22 (br., H_β−C(10)); 2.17 (br., H_β−C(9)); 2.12 (br., H_α−C(10)); 2.11 (br., H_β−C(13)); 2.02 (*dd*, *J* = 6.1, 17.4, H_α−C(13)); 1.87 (*m*, H_β−C(14)); 1.77 (*m*, H−C(7)); 1.73 (br., H_β−C(6)); 1.66 (br., H_α−C(14)); 1.64 (br., H_α−C(6)); 1.60 (br., H_α−C(9)); 1.59 (*s*, Me(20)); 1.56 (*m*, H−C(1)); 1.53 (*s*, Me(19)); 1.40 (*dd*, *J* = 5.7, 12.1, H_β−C(5)); 1.27 (*s*, Me(18)); 1.20 (*dt*, *J* = 6.7, 12.5, H_α−C(5)); 1.09 (*s*, Me(17)). ^{13}C-NMR (125 MHz, $CDCl_3$): 154.7 (*s*); 137.3 (*s*); 127.2 (*s*); 79.7 (*d*); 78.1 (*d*); 77.5 (*s*); 54.3 (*d*); 52.4 (*d*); 46.9 (*t*); 43.2 (*s*); 39.2 (*t*); 38.0 (*s*); 36.7 (*d*); 32.7 (*q*); 31.9 (*t*); 26.7 (*q*); 25.7 (*t*); 22.7 (*t*); 21.5 (*q*); 20.3 (*t*); 19.0 (*q*). HR-MS: 364.1801 ($C_{21}H_{29}ClO_3^{35+}$; calc. 364.1805). Anal. calc. for $C_{21}H_{29}ClO_3$: C 69.12, H 8.01; found: C 68.98, H 8.35.

8-Chloro-13-oxokempa-11-ene-2,3-diol 2,3-Carbonate (=*2a*RS,*3*SR,*8a*RS,*8b*RS,*11a*SR,*11b*RS,*11c*RS,*11d*SR*)-3-Chloro-1,2a,3,4,5,8,8a,8b,11a,11b,11c,11d-dodecahydro-3,6,11b,11d-tetramethylazuleno[1′,8′,7′:3,4,5]-naphtho[1,2-*d*][1,3]dioxole-7,10(2*H*)-dione*; **17**). Under N_2, a mixture of pyridinium dichromate (2.40 g, 6.38 mmol), 2M ^{t}BuOOH in 1,2-dichloroethane (3.0 ml, 5.90 mmol), and *Celite* (2.50 g) in benzene (30 ml) was vigorously stirred at 20° for 5 min. Then **16** (432 mg, 1.18 mmol) in benzene (30 ml) was added at once with stirring, and stirring was continued for 41 h at 20°. The mixture was diluted with Et_2O (150 ml) and passed through a pad of silica gel, the silica gel washed with AcOEt (300 ml), the combined org. phase condensed to 1/3 of the original volume, washed with sat. aq. $Na_2O_3S_2$ soln. (3 × 30 ml) and brine (3 × 30 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 3:1): 222 mg (50%) of **17** and 181 mg (42%) of

starting **16**. **17**: Colorless needles. M.p. 217–218° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 4.86 (*dd*, *J* = 5.0, 9.3, H–C(2)); 4.73 (*d*, *J* = 9.5, H–C(3)); 1.77 (*s*, Me(20)); 1.55 (*s*, Me); 1.33 (*s*, Me); 1.26 (*s*, Me). ^{13}C-NMR (125 MHz, $CDCl_3$): 196.9 (*s*); 163.8 (*s*); 154.1 (*s*); 131.4 (*s*); 79.1 (*d*); 76.2 (*s*); 76.1 (*d*); 55.0 (*d*); 51.8 (*d*); 45.6 (*t*); 43.6 (*s*); 40.2 (*s*); 39.1 (*t*); 36.2 (*d*); 34.7 (*t*); 32.5 (*q*); 27.0 (*q*); 25.9 (*t*); 24.9 (*t*); 18.9 (*q*); 11.0 (*q*). HR-MS: 378.1606 ($C_{21}H_{27}ClO_4^{35+}$; calc. 378.1598). Anal. calc. for $C_{21}H_{27}ClO_4$: C 66.57, H 7.18; found: C 66.50, H 7.00.

13-Oxokempa-7,11-diene-2,3-diol 2,3-Carbonate (=*(8a*RS,*8b*RS,*11a*SR,*11b*RS,*11c*RS,*11d*SR)*-1,4,5,8,8a,8b,11a,11b,11c,11d-Decahydro-3,6,11b,11d-tetramethylazuleno[1′,8′,7′:3,4,5]naphtho[1,2-*d*][1,3]dioxole-7,10(2*H*)-dione*; **18**). Under N_2, a mixture of **17** (661 mg, 1.74 mmol) and LiBr (779 mg, 8.97 mmol) in DMF (20 ml) was warmed at 105° for 15 h. After cooling to 20°, the mixture was poured into H_2O (100 ml), the aq. phase extracted with AcOEt (3 × 30 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue purified by CC (hexane/AcOEt 2:1): 439 mg (quant.) of **18**. M.p. 197–198° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 4.86 (*dd*, *J* = 4.6, 9.2, H–C(2)); 4.76 (*d*, *J* = 9.3, H–C(3)); 2.84 (br. *s*, H–C(16)); 1.76 (*s*, Me(20)); 1.57 (*s*, Me); 1.30 (*s*, Me); 1.28 (*s*, Me). ^{13}C-NMR (125 MHz, $CDCl_3$): 197.1 (*s*); 163.3 (*s*); 154.4 (*s*); 135.1 (*s*); 129.3 (*s*); 129.1 (*s*); 79.4 (*d*); 76.6 (*d*); 53.4 (*d*); 45.1 (*s*); 43.7 (*s*); 38.1 (*t*); 35.9 (*d*); 35.0 (*t*); 35.0 (*t*); 29.1 (*t*); 27.0 (*q*); 25.8 (*t*); 22.2 (*q*); 19.6 (*q*); 10.9 (*q*). HR-MS: 342.1840 ($C_{21}H_{26}O_4^+$; calc. 342.1831). Anal. calc. for $C_{21}H_{26}O_4$: C 73.66, H 7.65; found: C 73.50, H 7.47.

7,8-Epoxy-13-oxokemp-11-ene-2,3-diol 2,3-Carbonate (=*(3a*RS,*3b*RS,*9b*RS,*9c*RS,*11a*RS,*11b*SR)*-3a,3b,8,8a,9b,9c,10,11,11a,11b-Decahydro-6,8a,9c,11a-tetramethyl-4*H*-oxireno[2″,3″:3′a,4′]azuleno[1′,8′,7′:3,4,5]naphtho[1,2-*d*][1,3]dioxole-2,5(7*H*)-dione*; **19**). Under N_2, *m*-CPBA (430 mg, 2.49 mmol) and $NaHCO_3$ powder (1.09 g, 13.0 mmol) were added to a cooled CH_2Cl_2 soln. (15 ml) of **18** (439 mg, 1.28 mmol) at −40° with stirring, and stirring was continued for 18 h at −40°. The mixture was poured into sat. aq. $NaHCO_3$ soln. (15 ml), the aq. phase extracted with AcOEt (15 ml × 3), the combined org. phase successively washed with sat. aq. $Na_2O_3S_2$ soln. (3 × 10 ml), sat. aq. $NaHCO_3$ soln. (3 × 10 ml), and brine (3 × 15 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 2:1): 451 mg (98%) of **19**, 4:1 α/β-epoxy stereoisomer mixture. White powder. M.p. not measured. HR-MS: 358.1793 ($C_{21}H_{26}O_5^+$; calc. 358.1780).

2,3-Dihydroxykempa-7,11-dien-13-one (=*(2a*RS,*3*RS,*4*RS,*4a*RS,*10b*RS,*10c*RS)*-1,2,2a,3,4,4a,5,6,8,9,10b,10c-Dodecahydro-3,4-dihydroxy-2a,7,10,10c-tetramethylnaphth[2,1,8-*cde*]azulen-6-one*; **20a**). Under N_2, **18** (10 mg, 29 μmol) in 2M KOH/MeOH (10 ml) was stirred for 15 min at 20°, then poured into H_2O (20 ml). The aq. phase was extracted with AcOEt (3 × 15 ml), the org. phase dried (Na_2SO_4) and evaporated, and the residue purified by CC (hexane/AcOEt 2:1): 8 mg (87%) of **20a**. M.p. not measured. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.85 (br. *s*, H–C(2)); 3.50 (br. *s*, H–C(3)); 3.01 (br. *s*, H–C(16)); 1.77 (*s*, Me(20)); 1.54 (*s*, Me); 1.45 (*s*, Me); 1.39 (*s*, Me). HR-MS: 316.2008 ($C_{20}H_{28}O_3^+$; calc. 316.2038).

2α-Hydroxy-3α-(methoxymethoxy)kempa-7,11-dien-13-one (=*(2a*RS,*3*RS,*4*RS,*4a*RS,*10b*RS,*10c*RS)*-1,2,2a,3,4,4a,5,6,8,9,10b,10c-Dodecahydro-4-hydroxy-3-(methoxymethyl)-2a,7,10,10c-tetramethylnaphth[2,1,8-*cde*]azulen-6-one*; **20b**). Under N_2, a mixture of **20a** (11 mg, 0.035 mmol), ^{i}Pr$_2$NEt (56 μl, 0.32 mmol) and $MeOCH_2Cl$ (12 μl, 0.15 mmol) in CH_2Cl_2 (2 ml) was stirred at 20° for 48 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 × 10 ml), the combined org. phase washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 6:1): 12 mg (quant.) of **20b**. White powder (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.42 (*s*, Me); 1.48 (*s*, Me); 1.54 (*s*, Me); 1.77 (*s*, Me); 1.86 (*ddd*, *J* = 2.9, 5.2, 12.5, 1 H); 2.04 (*ddd*, *J* = 2.4, 4.0, 14.4, 1 H); 2.32 (*dd*, *J* = 4.8, 18.0, 1 H); 2.42 (br. *d*, *J* = 16.8, 1 H); 2.48 (*dt*, *J* = 12.2, 4.0, 1 H); 2.70 (*dt*, *J* = 4.2, 13.0, 1 H); 2.98 (*s*, 1 H); 3.01 (*dd*, *J* = 14.4, 18, 1 H); 3.38 (*d*, *J* = 3.1, H–C(3)); 3.45 (*s*, MeO); 3.93 (*t*, *J* = 3.1, H–C(2)); 4.68, 4.80 (2*d*, each *J* = 7.1, MeOC*H*$_2$O). ^{13}C-NMR (125 MHz, $CDCl_3$): 10.8 (*q*); 22.2 (*q*); 23.3 (*q*); 25.8 (*q*); 26.1 (*t*); 31.0 (*t*); 36.1 (*t*); 38.1 (*t*); 38.2 (*t*); 39.7 (*d*); 45.1 (*s*); 47.5 (*s*); 56.1 (*q*); 57.1 (*d*); 71.9 (*d*); 79.1 (*d*); 96.5 (*t*); 126.6 (*s*); 127.3 (*s*); 135.3 (*s*); 168.6 (*s*); 199.3 (*s*). HR-MS: 360.2316 ($C_{22}H_{32}O_4^+$; calc. 360.2301). Anal. calc. for $C_{22}H_{32}O_4$: C 73.30, H 8.95; found: C 73.50, H 8.64.

Data of O-*[(2a*RS,*3*SR,*4*RS,*4a*RS,*10b*RS,*10*SR)*-1,2,2a,3,4,4a,5,6,8,9,10b,10c-Dodecahydro-3-(methoxymethoxy)-2a,7,10,10c-tetramethyl-6-oxonaphth[2,1,8-*cde*]azulen-4-yl]* S-*Methyl Carbonodithioate* (**20c**): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.44 (*s*, Me), 1.45 (*s*, Me); 1.56 (*s*, Me); 1.76 (*s*, Me); 2.60 (*s*, MeS); 3.06 (*s*, H–C(16)); 3.41 (*s*, MeO); 3.63 (*d*, *J* = 3.6, H–C(3)); 4.44, 4.85 (2*d*, each *J* = 7.3, MeOC*H*$_2$O); 6.34 (*dd*, *J* = 2.4, 3.4, H–C(2)). HR-MS: 450.1890 ($C_{24}H_{34}O_4S_2^+$; calc. 450.1899).

*Data of (2a*RS,*3*RS,*4a*RS,*10b*RS,*10c*RS)*-2,2a,3,4,4a,5,8,9,10b,10c-Decahydro-3-(methoxymethoxy)-2a,7,10,10c-tetramethylnaphth[2,1,8-*cde*]azulen-6(1*H*)-one* (**20d**): ^{1}H-NMR (400 MHz, $CDCl_3$): 1.23 (*s*, Me); 1.24 (*s*, Me); 1.59 (*s*, Me); 1.76 (*s*, Me); 2.81 (br. *s*, H–C(16)); 3.40 (*s*, MeO); 3.50 (*t*, *J* = 8, H–C(3)); 4.60, 4.75 (2*d*, each *J* = 7.0, MeOC*H*$_2$O). HR-MS: 344.2339 ($C_{22}H_{32}O_3^+$; calc. 344.2351).

*Data of (8a*RS,*10*RS,*10a*RS,*10b*SR,*10c*RS*)-1,4,5,8,8a,9,10,10a,10b,10c-Decahydro-10-(methoxymethoxy)-3a,6,10a,10c-tetramethyl-2*H*-naphth[1′,7′,8′:7,8,1]azuleno[3a,4-*b*]oxiren-7(3a*H*)-one* (**21**). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.18 (*s*, Me); 1.28 (*s*, Me); 1.35 (*s*, Me); 1.77 (*s*, Me); 3.40 (*s*, MeO); 3.52 (*dd*, *J* = 5.8, 11.0, H−C(3)); 4.60, 4.76 (2*d*, each *J* = 6.9, MeOCH_2O). HR-MS: 360.2346 ($C_{22}H_{32}O_4^+$; calc. 360.2301).

7α,8α-Epoxy-13-oxokempane-2,3-diol 2,3-Carbonate (= *(3a*RS,*3b*RS,*6*SR,*6a*SR,*8a*SR,*9a*RS,*9b*RS,*9c*RS,*11a*RS,*11b*-SR*)-3a,3b,6,6a,8,8a,9b,9c,10,11,11a,11b-Dodecahydro-6,8a,9c,11a-tetramethyl-4*H*-oxireno[2″,3″:3′a,4′]azuleno[1′,8′,7′:3,4,5]naphtho[1,2-*d*][1,3]dioxole-2,5(7*H*)-dione* (**25**). An EtOH soln. (4 ml) of **19a**/**19b** (4 : 1; 151 mg, 421 μmol) was stirred under H_2 in the presence of 5% Pd/C (303 mg) and $NaHCO_3$ (363 mg, 4.32 mmol) for 72 h at r.t. The mixture was diluted with CH_2Cl_2 (30 ml) before passing through a pad of silica gel, the silica gel washed with AcOEt (50 ml); the combined org. phase evaporated, and the residue purified by CC (hexane/AcOEt 1 : 1): 118 mg (77%) of **22**/**23** (white powder) and 30 mg (20%) of unreacted **19b**. A CH_2Cl_2 soln. (3 ml) of **22**/**23** (17 mg, 46.9 μmol) was added dropwise into a stirred *Dess–Martin* periodinane (45 mg, 106 μmol) soln. in CH_2Cl_2 (1 ml) and pyridine (19 μl, 235 μmol), and the mixture was stirred for additional 20 min. After addition of sat. aq. solns. of $NaHCO_3$ and then $Na_2O_3S_2$ (10 ml each), the aq. phase was extracted with AcOEt (3 × 10 ml), and the combined org. layer successively washed with sat. aq. $Na_2O_3S_2$ soln. (3 × 10 ml), sat. aq. $NaHCO_3$ soln. (3 × 10 ml), and brine (3 × 15 ml), dried (Na_2SO_4), and evaporated: 17 mg of **24**/**25**. Under N_2, a MeOH soln. (1 ml) of **24**/**25** (17 mg, 47.2 μmol) and NaOMe (6 mg, 111 μmol) was kept at 0° for 1 h. Sat. aq. NH_4Cl soln. (5 ml) was added, the aq. phase extracted with AcOEt (3 × 10 ml), the combined org. phase successively washed with sat. aq. NH_4Cl soln. (2 × 10 ml) and brine (2 × 7 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 2 : 1): 15 mg (2 steps 89%) of **25**. M.p. 248–249° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 4.75 (*m*, H−C(2), H−C(3)); 2.82 (*t*, *J* = 14.0, H_α−C(14)); 2.33 (*m*, H−C(12), H_β−C(14)); 2.01 (*m*, H_β−C(9)); 1.92 (*m*, H_β−C(10)); 1.88 (*td*, *J* = 3.4, 14.0, H−C(1)); 1.83 (br., H_β−C(5)); 1.81 (*s*, H−C(16)); 1.80 (*m*, H−C(6)); 1.56 (*m*, H_α−C(9), H_α−C(10)); 1.47 (*m*, H−C(5)); 1.43 (*m*, H−C(11)); 1.43 (*s*, Me(18)); 1.26 (*s*, Me(19)); 1.21 (*s*, Me(17)); 1.09 (*d*, *J* = 6.5, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 209.8 (*s*); 154.0 (*s*); 79.3 (*d*); 77.3 (*d*); 73.7 (*s*); 60.2 (*s*); 58.5 (*d*); 49.9 (*d*); 46.5 (*d*); 44.5 (*s*); 41.8 (*d*); 40.0 (*t*); 36.7 (*s*); 35.1 (*t*); 33.4 (*t*); 28.4 (*q*); 27.9 (*t*); 26.4 (*t*); 18.1 (2*q*); 12.4 (*q*). HR-MS: 360.1930 ($C_{21}H_{28}O_5^+$; calc. 360.1937). Anal. calc. for $C_{21}H_{28}O_5$: C 69.98, H 7.83; found: C 69.75, H 7.92.

Data of α-Epoxy Derivative **19a**: ^{1}H-NMR (500 MHz, $CDCl_3$): 4.89 (*dd*, *J* = 4.6, 9.2, 1 H); 4.76 (*d*, *J* = 9.5, 1 H); 2.75 (*dd*, *J* = 14.4, 17.1, 1 H); 2.46 (*dd*, *J* = 4.0, 17.1, 1 H); 2.40 (*dt*, *J* = 13.4, 4.6, 1 H); 2.28 (*m*, 3 H); 2.17 (*dt*, *J* = 4.6, 13.1, 1 H); 1.81 (*s*, Me); 1.51 (*s*, Me); 1.23 (*s*, Me); 1.22 (*s*, Me). HR-MS: 358.1773 ($C_{21}H_{26}O_5^+$; calc. 358.1780).

Data of β-Epoxy Derivative **19b**: ^{1}H-NMR (500 MHz, $CDCl_3$): 4.91 (*dd*, *J* = 5.0, 9.0, 1 H); 4.79 (*d*, *J* = 9.2, 1 H); 2.78 (*dd*, *J* = 14.0, 17.0, 1 H); 2.68 (*dt*, *J* = 14.0, 4.6, 1 H); 2.43 (*s*, 1 H); 1.75 (*s*, Me); 1.39 (*s*, Me); 1.26 (*s*, Me); 1.18 (*s*, Me). HR-MS: 358.1779 ($C_{21}H_{26}O_5^+$; calc. 358.1780).

*Data of (3a*RS,*3b*RS,*5*SR,*6*RS,*6a*SR,*8a*SR,*9a*RS,*9b*RS,*9c*RS,*11a*RS,*11b*SR*)-3a,3b,5,6,6a,7,8,8a,9b,9c,10,11,11a,11b-Tetradecahydro-5-hydroxy-6,8a,9c,11a-tetramethyl-4*H*-oxireno[2″,3″:3′a,4′]azuleno[1′,8′,7′:3,4,5]-naphtho[1,2-*d*][1,3]dioxol-2-one* **22**: ^{1}H-NMR (500 MHz, $CDCl_3$): 4.84 (*dd*, *J* = 4.2, 9.3, 1 H); 4.70 (*d*, *J* = 9.5, 1 H); 3.79 (*td*, *J* = 4.9, 11.9, 1 H); 1.40 (*s*, Me); 1.28 (*s*, Me); 1.00 (*s*, Me); 0.95 (*d*, *J* = 7.3, Me). ^{13}C-NMR (125 MHz, $CDCl_3$): 154.5 (*s*); 79.5 (*d*); 78.2 (*d*); 74.4 (*s*); 73.6 (*d*); 60.2 (*s*); 60.1 (*d*); 44.2 (*s*); 43.3 (*d*); 41.1 (*d*); 40.8 (*d*); 36.3 (*s*); 35.7 (*t*); 33.6 (*t*); 28.9 (*q*); 28.7 (*t*); 28.5 (*t*); 26.4 (*t*); 20.9 (*q*); 18.4 (*q*); 9.0 (*q*). HR-MS: 362.2085 ($C_{21}H_{30}O_5^+$; calc. 362.2093).

*Data of (3a*RS,*3b*RS,*5*SR,*6*SR,*6a*SR,*8a*SR,*9a*RS,*9b*RS,*9c*RS,*11a*RS,*11b*SR*)-Isomer* **23** (see **22**): ^{1}H-NMR (400 MHz, $CDCl_3$): 4.80 (*dd*, *J* = 4.4, 9.3, 1 H); 4.70 (*d*, *J* = 9.5, 1 H); 3.17 (*m*, 1 H); 1.41 (*s*, Me); 1.28 (*s*, Me); 1.07 (*d*, *J* = 6.3, Me); 0.99 (*s*, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 154.4 (*s*); 79.4 (*d*); 78.2 (*d*); 74.9 (*d*); 74.1 (*s*); 60.4 (*s*); 58.6 (*d*); 47.0 (*d*); 44.4 (*s*); 41.4 (*d*); 39.2 (*d*); 36.3 (*s*); 35.3 (*t*); 33.4 (*t*); 33.3 (*t*); 28.6 (*q*); 28.2 (*t*); 25.3 (*t*); 18.8 (*q*); 18.2 (*q*); 16.2 (*q*). HR-MS: 362.2077 ($C_{21}H_{30}O_5^+$; calc. 362.2093).

*Data of (3a*RS,*3b*RS,*6*RS,*6a*SR,*8a*SR,*9a*RS,*9b*RS,*9c*RS,*11a*RS,*11b*SR*)-Isomer* **24** (see **25**). ^{1}H-NMR (500 MHz, $CDCl_3$): 1.87 (*m*, H−C(1)); 4.80 (*dd*, *J* = 4.1, 9.3, H−C(2)); 4.70 (*d*, *J* = 4.5, H−C(3)); 2.46 (*quint.*, *J* = 6.8, H−C(12)); 2.20 (br. *d*, *J* = 14.6, 1 H−C(14)); 3.00 (*t*, *J* = 14.4, 1 H−C(14)); 1.71 (*s*, H−C(16)); 1.20 (*s*, Me(17)); 1.43 (*s*, Me(18)); 1.26 (*s*, Me(19)); 1.17 (*d*, *J* = 7.0, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 44.1 (*d*, C(1)); 77.3 (*d*, C(2)); 79.4 (*d*, C(3)); 44.4 (*s*, C(4)); 35.4 (*t*, C(5)); 28.3 (*t*, C(6)); 60.0 (*s*, C(7)); 74.0 (*s*, C(8)); 33.4 (*t*, C(9)); 25.1 (*t*, C(10)); 41.9 (*d*, C(11)); 50.4 (*d*, C(12)); 212.7 (*s*, C(13)); 36.7 (*t*, C(14)); 36.4 (*s*, C(15)); 59.8 (*d*, C(16)); 20.2 (*q*, C(17)); 28.6 (*q*, C(18)); 18.4 (*q*, C(19)); 14.1 (*q*, C(20)); 154.5 (*s*, CO). HR-MS: 360.1920 ($C_{21}H_{28}O_5^+$; calc. 360.1937).

7α,8α-Epoxykempane-2,3,13α-triol 2,3-Carbonate (= *(3a*RS,*3b*RS,*5*SR,*6*SR,*6a*RS,*8a*SR,*9a*RS,*9b*RS,*9c*RS,*11a*RS,*11b*SR*)-Isomer* (see above); **23**). To a stirred MeOH soln. (3 ml) of epoxy ketone **25** (53 mg, 147 μmol)

was added $NaBH_4$ (16 mg, 441 μmol) at −30°, and the mixture was stirred for 3 h. After dilution with brine (10 ml), the mixture was extracted with AcOEt (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 2:1): 47 mg (88%) of **23**. White powder. M.p. 245–246° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 4.81 (*dd*, *J* = 4.3, 9.2, H−C(2)); 4.70 (*d*, *J* = 9.2, H−C(3)); 3.16 (*dt*, *J* = 5.2, 10.4, H−C(13)); 1.69 (br. *s*, H−C(16)); 1.40 (*s*, Me(18)); 1.27 (*s*, Me(19)); 1.06 (*d*, *J* = 6.1, Me(20)); 0.99 (*s*, Me(17)). HR-MS: 362.2107 ($C_{21}H_{30}O_5^+$; calc. 362.2093). Anal. calc. for $C_{21}H_{30}O_5$: C 69.59, H 8.34; found: C 69.80, H 8.45.

7α,8α-Epoxy-13α-[(methylthio)thioxomethoxy]kempane-2,3-diol 2,3-Carbonate (= S-*Methyl* O-*[(3a*RS,*3b*RS,*5*SR,*6*SR,*6a*SR,*8a*SR,*9a*RS,*9b*RS,*9c*RS,*11a*RS,*11b*SR*)-3a,3b,5,6,6a,7,8,8a,9b,9c,10,11,11a,11b-Tetradecahydro-6,8a,9c,11a-tetramethyl-2-oxo-4*H-*oxireno[2″,3″:3′a,4′]azuleno[1′,8′,7′:3,4,5]naphtho[1,2-*d*][1,3]dioxol-5-yl] Carbonodithioate*). Under N_2, **23** (47 mg, 130 μmol) in THF (3 ml) was added to a stirred THF soln. (1 ml) of NaH (35 mg, 1.30 mmol) at 0°, and the mixture was stirred for 1 h at 0°. After CS_2 (39 μl, 650 μmol) was added, the temp. was raised to 25° before MeI (40 μl, 650 μl) was added dropwise, and the mixture was stirred for 23 h. After dilution with sat. aq. NH_4Cl soln. (15 ml), the mixture was extracted with Et_2O (3 × 10 ml), the combined org. phase washed with sat. aq. NH_4Cl soln. (2 × 5 ml) and then brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 5:1): 56 mg (95%) of *S*-methyl carbonodithioate of **23**. Yellow powder. M.p. 207–208° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 5.27 (*dt*, *J* = 5.2, 11, H−C(13)); 4.80 (*dd*, *J* = 4.3, 9.5, H−C(2)); 4.71 (*d*, *J* = 9.2, H−C(3)); 2.57 (*s*, CS_2Me); 2.16 (*ddd*, *J* = 2.5, 5.2, 13, 1 H); 1.71 (br. *s*, H−C(16)); 1.41 (*s*, Me(19)); 1.28 (*s*, Me(18)); 1.04 (*s*, Me(17)); 0.96 (*d*, *J* = 6.5, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 216.2 (*s*, *C*S_2Me); 154.3 (*s*, C=O); 86.2 (*d*, C(13)); 79.4 (*d*, C(3)); 77.9 (*d*, C(2)); 74.0 (*s*); 60.3 (*s*); 58.6 (*d*); 47.2 (*d*); 44.5 (*s*); 38.9 (*d*); 38.2 (*d*); 36.3 (*s*); 35.3 (*t*); 33.4 (*t*); 28.6 (*q*, Me(18)); 28.3 (*t*); 28.2 (*t*); 25.4 (*t*); 19.0 (*q*, CS_2*Me*); 18.7 (*q*); 18.2 (*q*); 16.2 (*q*, Me(20)). HR-MS: 452.1678 ($C_{23}H_{32}O_5S_2^+$; calc. 452.1691). Anal. calc. for $C_{23}H_{32}O_5S_2$: C 61.03, H 7.13; found: C 60.88, H 7.46.

7α,8α-Epoxykempane-2,3-diol 2,3-Carbonate (= *(3a*RS,*3b*RS,*6*RS,*6a*SR,*8a*SR,*9a*RS,*9b*RS,*9c*RS,*11a*RS,*11b*SR*)-3a,3b,5,6,6a,7,8,8a,9b,9c,10,11,11a,11b-Tetradecahydro-6,8a,9c,11a-tetramethyl-4*H-*oxireno[2″,3″:3′a,4′]azuleno[1′,8′,7′:3,4,5]naphto[1,2-*d*][1,3]dioxol-2-one*; **26**). Under N_2, a mixture of methyl carbonodithioate of **23** (56 mg, 124 μmol), Ph_3SnH (65 μl, 248 μmol), and 2,2′-azobis[isobutyronitrile] (AIBN) (cat.) in toluene (3 ml) was refluxed for 1 h. Then H_2O (20 ml) was added at 20°, the aq. phase extracted with AcOEt (3 × 5 ml), the combined org. layer washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 5:1): 26 mg (61%) of **26**. Colorless needles (hexane). M.p. 247–248°. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.79 (*dd*, *J* = 4.3, 9.2, H−C(2)); 4.69 (*d*, *J* = 9.5, H−C(3)); 1.67 (br. *s*, H−C(16)); 1.40 (*s*, Me(19)); 1.27 (*s*, Me(18)); 0.96 (*s*, Me(17)); 0.91 (*d*, *J* = 6.4, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 154.7 (*s*, C=O); 79.6 (*d*, C(3)); 78.7 (*d*, C(2)); 74.4 (*s*); 60.4 (*s*); 58.9 (*d*); 48.8 (*d*); 44.3 (*s*); 41.9 (*d*); 36.7 (*s*); 36.1 (*t*); 35.3 (*t*); 33.6 (*t*); 33.3 (*d*); 28.6 (*q*); 28.2 (*t*); 25.4 (*t*); 24.4 (*t*); 21.5 (*q*, Me(20)); 18.7 (*q*); 18.2 (*q*). HR-MS: 346.2143 ($C_{21}H_{30}O_4^+$; calc. 346.2144). Anal. calc. for $C_{21}H_{30}O_4$: C 72.80, H 8.73; found: C 72.53, H 8.48.

7α,8α-Epoxykempane-2,3-diol (= *(2a*RS,*3a*SR,*5a*SR,*6*RS,*8a*RS,*9*RS,*10*SR,*10a*RS,*10b*RS,*10c*RS*)-1,3a,4,5,5a,6,7,8,8a,9,10,10a,10b,10c-Tetradecahydro-3a,6,10a,10c-tetramethyl-2*H-*naphth[1′,7′,8′:7,8,1]azuleno[3a,4-*b*]oxirene-9,10-diol*; **27**). At 20°, **26** (22 mg, 63.5 μmol) in 2M KOH/MeOH (5 ml) was stirred for 12 h. The mixture was diluted with H_2O (20 ml) and extracted with Et_2O (3 × 10 ml), the combined org. layer washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 2:1): 20 mg (98%) of **27**. White solid. M.p. 168–169° (hexane). ^{1}H-NMR (500 MHz, $CDCl_3$): 4.03 (*t*, *J* = 6.5, H−C(2)); 3.86 (*d*, *J* = 7.7, H−C(3)); 1.85 (br. *s*, H−C(16)); 1.34 (*s*, Me(19)); 1.26 (*s*, Me(18)); 1.05 (*s*, Me(17)); 0.89 (*d*, *J* = 6.4, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 75.1 (*s*); 71.4 (*d*); 69.6 (*d*); 60.9 (*s*); 59.2 (*d*); 49.8 (*d*); 46.6 (*s*); 44.3 (*d*); 38.1 (*s*); 36.5 (*t*); 34.5 (*t*); 34.4 (*t*); 32.9 (*d*); 29.2 (*t*); 29.1 (*q*); 24.4 (2*t*); 21.6 (*q*); 18.8 (*q*); 18.3 (*q*). HR-MS: 320.2330 ($C_{20}H_{32}O_3^+$; calc. 320.2351). Anal. calc. for $C_{20}H_{32}O_3$: C 74.96, H 10.06; found: C 75.10, H 10.25.

7α,8α-Epoxy-2(3)-hydroxykempan-3(2)-yl Pivalate (= *(2a*RS,*3a*SR,*5a*SR,*6*RS,*8a*RS,*9*RS,*10*SR,*10a*RS,*10b*RS,*10c*RS*)-1,3a,4,5,5a,6,7,8,8a,9,10,10a,10b,10c-Tetradecahydro-9(10)-hydroxy-3a,6,10a,10c-tetramethyl-2*H-*naphth[1′7′,8′:7,8,1]azuleno[3a,4-*b*]oxiren-10(9)-yl 2,2-Dimethylpropanoate*; **28**/**29** 1:1). Under N_2, pivalic anhydride (34 μl, 165 μmol) was added to a stirred mixture of **27** (21 mg, 66 μmol) and NaH (20 mg, 833 μmol) in THF (3 ml) at 0°, and stirring was continued for 30 min at 0°. The mixture was diluted with sat. aq. NH_4Cl soln. (10 ml) and extracted wtih Et_2O (3 × 10 ml), the combined org. layer washed with sat. aq. NH_4Cl soln. (3 × 5 ml) and brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 5:1): 25 mg (94%) of **28**/**29** 1:1. FC (hexane/AcOEt 7:1) provided small amounts of each compound.

Data of **28**: White powder. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.12 (*d*, *J* = 7.3, H−C(3)); 4.15 (*dd*, *J* = 6.1, 7.3, H−C(2)); 1.28 (*s*, Me); 1.26 (*s*, Me); 1.25 (*s*, Me_3CCO); 1.10 (*s*, Me); 0.91 (*d*, *J* = 6.4, Me(20)). HR-MS: 404.2905 ($C_{25}H_{40}O_4^+$; calc. 404.2927).

Data of **29**: White powder. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.15 (*dd*, *J* = 5.5, 7.0, H–C(2)); 3.93 (*d*, *J* = 7.0, H–C(3)); 1.33 (*s*, Me); 1.28 (*s*, Me); 1.25 (*s*, Me_3CCO); 1.10 (*s*, Me); 0.90 (*d*, *J* = 6.4, Me(20)). HR-MS: 404.2910 ($C_{25}H_{40}O_4^+$; calc. 404.2927).

7α,8α-Epoxy-2(3)-oxokempan-3(2)α-yl Pivalate (= *(2a*RS,*3a*SR,*5a*SR,*6*RS,*8a*RS,*10*SR*(9*RS*),10a*RS,*10b*RS,*10c*SR-*(10c*RS*))-1,3a,4,5,5a,6,7,8,8a,9,10,10a,10b,10c-Tetradecahydro-3a,6,10a,10c-tetramethyl-9(10)-oxo-2*H-*naphth[1′,7′,8′:7,8,1]azuleno[3a,4-*b*]oxiren-10(9)-yl 2,2-Dimethylpropanoate*; **30a**/**31a** 1:1). A CH_2Cl_2 soln. (2 ml) of **28**/**29** 1:1 (26 mg, 64.3 μmol) was added to a stirred *Dess-Martin* periodinane (84 mg, 199 μmol) soln. in CH_2Cl_2 (1 ml) and pyridine (26 μl, 322 μmol), and the mixture was stirred for 20 min. Sat. aq. solns. of $NaHCO_3$ and then $Na_2O_3S_2$ (10 ml each) were added. Then, the aq. phase was extracted with AcOEt (3 × 10 ml), the combined org. phase successively washed with sat. aq. $Na_2O_3S_2$ soln. (3 × 10 ml), sat. aq. $NaHCO_3$ soln. (3 × 10 ml), and brine (3 × 10 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 8:1): 23 mg of **30a**/**31a** 1:1). HR-MS: 402.2778 ($C_{25}H_{38}O_4^+$; calc. 402.2770).

7α,8α-Epoxy-2-oxokempan-3β-yl Pivalate (= *(2a*RS,*3a*SR,*5a*SR,*6*RS,*8a*RS,*10*RS,*10a*RS,*10b*RS,*10c*SR*)-1,3a,4,5,5a,6,7,8,8a,9,10,10a,10b,10c-Tetradecahydro-3a,6,10a,10c-tetramethyl-9-oxo-2*H-*naphth[1′,7′,8′:7,8,1]azuleno[3a,4-*b*]oxiren-10-yl 2,2-Dimethylpropanoate*; **30b**). At 20°, **30a**/**31a** 1:1 (23 mg, 57 μmol) and NaOMe (23 mg, 426 μmol) in MeOH (3 ml) were stirred at 20° for 3 days. Then sat. aq. NH_4Cl soln. (10 ml) was added, the mixture extracted with AcOEt (3 × 10 ml), the combined org. phase washed with sat. aq. NH_4Cl soln. (3 × 10 ml) and brine (3 × 10 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 8:1): 19 mg (2 steps 73%) of **30b**. Colorless needles (hexane). M.p. 201–202°. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.42 (*s*, H–C(3)); 1.91 (br. *s*, H–C(16)); 1.31 (*s*, Me(19)); 1.29 (*s*, Me(18)); 1.27 (*s*, Me_3CCO); 1.00 (*s*, Me(17)); 0.92 (*d*, *J* = 6.1, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 206.3 (*s*); 177.9 (*s*); 77.8 (*d*); 73.9 (*s*); 62.8 (*d*); 60.1 (*s*); 54.7 (*d*); 48.4 (*d*); 45.6 (*s*); 39.0 (*s*); 38.3 (*s*); 35.3 (*t*); 34.1 (*t*); 33.7 (*t*); 32.4 (*d*); 29.8 (*t*); 29.0 (*q*); 27.2 (3*q*); 24.4 (*t*); 21.7 (*t*); 21.5 (*q*); 20.7 (*q*); 18.5 (*q*). HR-MS: 402.2759 ($C_{25}H_{38}O_4^+$; calc. 402.2770). Anal. calc. for $C_{25}H_{38}O_4$: C 74.59, H 9.51; found: C 74.50, H 9.55.

7α,8α-Epoxy-2(3)-hydroxy-13-oxokempan-3(2)yl Pivalates (= *(2a*RS,*3a*SR,*5a*SR,*6*SR,*8a*RS,*9*RS,*10*SR,*10a*RS,*10b*RS,*10c*RS*)-1,3a,4,5,5a,6,7,8,8a,9,10,10a,10b,10c-Tetradecahydro-9(10)-hydroxy-3a,6,10a,10c-tetramethyl-7-oxo-2*H-*naphth[1′,7′,8′:7,8,1]azuleno[3a,4-*b*]oxiren-10(9)-yl 2,2-Dimethylpropanoate*; **33**). Under N_2, pivalic anhydride (38 μl, 190 μmol) was added to a stirred mixture of **32** (40 mg, 0.12 mmol) and NaH (25 mg, 0.63 mmol) in THF (5 ml) at 0°, and the stirring was continued for 30 min at 0°. The mixture was diluted with sat. aq. NH_4Cl soln. (20 ml) and extracted with Et_2O (3 × 10 ml), the combined org. phase washed with sat. aq. NH_4Cl soln. (3 × 5 ml) and brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 4:1): 40 mg (80%) of **33**/**34** 3:2. FC (hexane/AcOEt 7:1) provided a small amount of **33** (the major component). White powder. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.10 (*d*, *J* = 7.6, H–C(3)); 4.13 (*t*, *J* = 7.2, H–C(2)); 2.80 (*t*, *J* = 14.2, 1 H–C(14)); 2.24 (*dd*, *J* = 3.4, 14.4, H–C(14)); 1.33 (*s*, Me); 1.29 (*s*, Me); 1.26 (*s*, Me_3CCO); 1.26 (*s*, Me); 1.08 (*d*, *J* = 6.7, Me(20)). HR-MS: 418.2707 ($C_{25}H_{38}O_5^+$; calc. 418.2719).

7α,8α-Epoxykemp-14-ene-2,13-dione (= *(2a*RS,*3a*SR,*5a*SR,*6*SR,*10a*SR,*10b*SR,*10c*SR*)-1,2,4,5,5a,6,10,10a,10b,10c-Decahydro-3a,6,10a,10c-tetramethyl-9*H-*naphth[1′,7′,8′:7,8,1]azuleno[3a,4-*b*]oxirene-7,9(3*H*)-dione*; **37**). Under N_2, a soln. of **33** (40 mg, 0.096 mmol) in CH_2Cl_2 (3 ml) was added dropwise to a clear *Dess–Martin* periodinane (81 mg, 0.19 mmol) soln. in CH_2Cl_2 (2 ml) and pyridine (39 μl, 0.48 mmol) with stirring, and the mixture was stirred for 1 h. Sat. aq. solns. of $NaHCO_3$ and then $Na_2O_3S_2$ (10 ml each) were added, and the mixture was stirred for 10 min. The aq. phase was extracted with AcOEt (3 × 10 ml) and the combined org. layer washed with sat. aq. $Na_2O_3S_2$ soln. (3 × 10 ml), sat. aq. $NaHCO_3$ soln. (3 × 10 ml), and brine (3 × 15 ml), dried (Na_2SO_4), and evaporated: 38 mg (96%) of **35**. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.10 (*d*, *J* = 6.4, Me(20)); 1.15 (*s*, Me); 1.25 (*s*, Me_3CCO); 1.27 (*s*, Me); 1.31 (*s*, Me); 2.51 (*dd*, *J* = 4.6, 14.9, 1 H–C(14)); 2.59 (*dd*, *J* = 12.5, 14.4, 1 H–C(14)); 2.85 (*dd*, *J* = 4.6, 12.5, H–C(1)); 5.23 (*s*, H–C(3)).

Under N_2, a MeOH soln. (3 ml) of **35** (38 mg, 91 μmol) and NaOMe (25 mg, 0.046 mmol) was kept at 20° for 30 h. Then sat. aq. NH_4Cl soln. (5 ml) was added, the aq. phase extracted with AcOEt (3 × 10 ml), the combined org. layer washed with sat. aq. NH_4Cl soln. (2 × 7 ml) and brine (2 × 7 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 4:1): 27 mg (93%) of **37**. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.20 (*d*, *J* = 6.8, Me(20)); 1.26 (*s*, Me); 1.28 (*s*, Me); 1.31 (*s*, Me); 2.36 (*qd*, *J* = 6.7, 12.2, H–C(12)); 2.60 (*d*, *J* = 18.0, 1 H–C(3)); 2.70 (*d*, *J* = 18, 1 H–C(3)); 6.60 (*s*, H–C(14)). ^{13}C-NMR (125 MHz, $CDCl_3$): 12.1 (*q*); 18.4 (*q*); 24.1 (*q*); 25.5 (*t*); 28.5 (*t*); 29.5 (*q*); 33.5 (*t*); 35.5 (*t*); 40.3 (*s*); 42.2 (*s*); 43.3 (*d*); 45.3 (*d*); 46.6 (*t*); 60.1 (*s*); 62.2 (*d*); 73.6 (*s*); 127.4 (*d*); 155.6 (*s*); 200.5 (*s*); 200.9 (*s*). HR-MS: 314.1892 ($C_{20}H_{26}O_3^+$; calc. 314.1882).

7α,8α-Epoxykempane-2,13-dione (= *(2a*RS,*3a*SR,*5a*SR,*6*SR,*8a*RS,*10a*SR,*10b*SR,*10c*RS*)-1,2,3,5,5a,6,8,8a,10,10a,10b,10c-Dodecahydro-3a,6,10a,10c-tetramethyl-9*H-*naphth[1′,7′,8′:7,8,1]azuleno[3a,4-*b*]oxirene-7,9(3*H*)-dione*; **38**). A MeOH soln. (5 ml) of **37** (27 mg, 0.086 mmol) was stirred under H_2 in the presence of 5%

Pd/C (54 mg) and $NaHCO_3$ (36.3 mg, 0.43 mmol) for 15 min at 20°. The mixture was diluted with CH_2Cl_2 (30 ml) and then passed through a pad of silica gel, the silica gel washed with AcOEt (50 ml), the combined org. phase evaporated, and the residue purified by CC (hexane/AcOEt 4:1): 18 mg (67%) of **38**. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.64 (*dd*, *J* = 4.0, 12.2, H–C(1)); 2.38 (*d*, *J* = 19.8, H–C(3)); 2.56 (*d*, *J* = 19.8, H–C(3)); 2.30 (*qd*, *J* = 6.8, 12.3, H–C(12)); 2.43 (*dd*, *J* = 12.5, 13.5, 1 H–C(14)); 2.68 (*dd*, *J* = 4.3, 13.7, 1 H–C(14)); 1.74 (br. *s*, H–C(16)); 1.07 (*s*, Me(17)); 1.31 (*s*, Me(18)); 1.29 (*s*, Me(19)); 1.09 (*d*, *J* = 6.8, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 53.7 (*d*, C(1)); 209.8 (*s*, C(2)); 47.3 (*t*, C(3)); 42.0 (*s*, C(4)); 38.2 (*t*, C(5)); 29.4 (*t*, C(6)); 60.0, 74.2 (2*s*, C(7), C(8)); 25.8, 33.8 (2*t*, C(9), C(10)); 49.2 (*d*, C(11)); 45.7 (*d*, C(12)); 211.3 (*s*, C(13)); 37.5 (*t*, C(14)); 40.0 (*s*, C(15)); 61.1 (*d*, C(16)); 19.2 (*q*, C(17)); 32.6 (*q*, C(18)); 18.2 (*q*, C(19)); 12.4 (*q*, C(20)). HR-MS: 316.2042 ($C_{20}H_{28}O_3^+$; calc. 316.2038). Anal. calc. for $C_{20}H_{28}O_3$: C 75.91, H 8.92; found: C 75.86, H 9.00.

7α,8α-Epoxy-2β-hydroxykempan-3β-yl Pivalate (=*(2a*RS,*3a*SR,*5a*SR,*6*RS,*8a*RS,*9*SR,*10*RS,*10a*RS,*10b*RS,*10c*RS*)-1,3a,4,5,5a,6,7,8,8a,9,10,10a, 10b,10c-Tetradecahydro-9-hydroxy-3a,6,10a,10c-tetramethyl-2*H*-naphth-[1′,7′,8′:7,8,1]azuleno[3a,4-*b*]oxiren-10-yl 2,2-Dimethylpropanoate*; **39**). To a stirred soln. of **30b** (8 mg, 19.9 μmol) in MeOH (3 ml) was added $NaBH_4$ (6 mg, 159 μmol) at −30°, and the mixture was stirred for 21 h at 25°. The mixture was diluted with H_2O (20 ml), the aq. phase extracted with Et_2O (10 ml × 3), the combined org. phase washed with brine (5 ml × 3), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 10:1): 7 mg (87%) of **39**. White solid. M.p. not measured. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.73 (*d*, *J* = 4.5, H–C(3)); 3.76 (*s*, OH); 3.73 (*t*, *J* = 5.2, H–C(2)); 1.27 (*s*, Me(19)); 1.26 (*s*, Me(18)); 1.25 (*s*, Me_3CCO); 1.02 (*s*, Me(17)); 0.91 (*d*, *J* = 5.2, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 181.2 (*s*); 87.0 (*d*); 75.1 (*d*); 74.4 (*s*); 63.4 (*d*); 60.2 (*s*); 48.5 (*d*); 45.6 (*s*); 44.7 (*d*); 39.1 (*s*); 38.4 (*s*); 36.5 (*t*); 34.0 (*t*); 33.0 (*d*); 32.9 (*t*); 30.1 (*q*); 29.0 (*t*); 27.2 (3*q*); 24.6 (*t*); 24.2 (*t*); 21.7 (*q*); 20.3 (*q*); 18.4 (*q*). NOESY (500 MHz, $CDCl_3$): 4.73 (*d*, *J* = 4.5, H–C(3))/1.02 (*s*, Me(17)); 1.26 (*s*, Me(18)); 3.73 (*t*, *J* = 5.2, H–C(2)); 1.26 (*s*, Me(18)). HR-MS: 404.2905 ($C_{25}H_{40}O_4^+$; calc. 404.2927).

7α,8α-Epoxy-2β-[(methylthio)thioxomethoxy]kempan-3β-yl Pivalate (=*(2a*RS,*3a*SR,*5a*SR,*6*RS,*8a*RS,*9*SR,*10*RS,*10a*RS,*10b*RS,*10c*RS*)-1,3a,4,5,5a,6,7,8,8a,9,10,10a,10b,10c-Tetradecahydro-3a,6,10a,10c-tetramethyl-9-[(methylthio)thioxomethoxy]2-H-naphth[1′,7′,8′:7,8,1]azuleno[3a,4-*b*]oxiren-10-yl 2,2-Dimethylpropanoate*; **40**). Under N_2, **39** (8 mg, 19.8 μmol) in THF (1 ml) was added to a stirred soln. of NaH (7 mg, 292 μmol) in THF (1 ml) at 0°, and the mixture was stirred for 35 min. After CS_2 (7 μl, 116μmol) was added, the temp. was raised to 25° before MeI (7 μl, 112 μmol) was added dropwise, and then the mixture was stirred for 20 h. The mixture was diluted with sat. aq. NH_4Cl soln. (20 ml) and extracted with AcOEt (3 × 10 ml), the combined org. layer washed with sat. aq. NH_4Cl soln. (2 × 5 ml) and brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 25:1): 6 mg (98%) of **40**. White solid. M.p. not measured. ^{1}H-NMR (500 MHz, $CDCl_3$): 6.35 (*t*, *J* = 6.7, H–C(2)); 5.44 (*d*, *J* = 6.1, H–C(3)); 2.54 (*s*, CS_2Me); 1.28 (*s*, Me(19)); 1.19 (*s*, Me(18)); 1.17 (*s*, Me_3CCO); 1.07 (*s*, Me(17)); 0.90 (*d*, *J* = 6.4, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 216.4 (*s*); 177.5 (*s*); 84.9 (*d*); 78.1 (*d*); 73.9 (*s*); 63.3 (*d*); 60.1 (*s*); 48.5 (*d*); 46.0 (*s*); 45.3 (*d*); 38.8 (*s*); 38.2 (*s*); 35.8 (*t*); 34.0 (*t*); 32.7 (*d*); 32.4 (*t*); 29.3 (*t*); 29.1 (*q*); 27.2 (3*q*); 24.5 (*t*); 23.4 (*t*); 21.6 (*q*); 19.9 (*q*); 18.6 (*q*); 18.4 (*q*). HR-MS: 494.2500 ($C_{27}H_{42}O_4S_4^+$; calc. 494.2525).

7α,8α-Epoxykempan-3β-yl Pivalate (=*(2a*RS,*3a*SR,*5a*SR,*6*RS,*8a*SR,*10*SR,*10a*RS,*10b*RS,*10c*SR*)-1,3a,4,5,5a,6,7,8,8a,9,10,10a,10b,10c-Tetradecahydro-3a,6,10a,11c-tetramethyl-2*H*-naphth[1′,7′,8′:7,8,1]azuleno[3a,4-*b*]oxiren-10-yl 2,2-Dimethylpropanoate*; **41**). Under N_2, a mixture of **40** (6 mg, 12.1 μmol), Ph_3SnH (6 μl, 24.2 μmol), and AIBN (cat.) in toluene (3 ml) was refluxed for 3 h, and then H_2O (10 ml) was added at 20°. The aq. phase was extracted with AcOEt (3 × 5 ml), the combined org. phase washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 25:1): 6 mg (quant.) of **41**. White solid. M.p. not measured. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.94 (*dd*, *J* = 7.1, 9.5, H–C(3)); 1.79 (br. *s*, H–C(16)); 1.27 (*s*, Me(19)); 1.20 (*s*, Me_3CCO); 1.18 (*s*, Me(17)); 0.89 (*d*, *J* = 6.4, Me(20)); 0.84 (*s*, Me(18)). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.3 (*s*); 74.9 (*d*); 74.5 (*s*); 63.2 (*d*); 60.1 (*s*); 48.2 (*d*); 47.0 (*s*); 39.1 (*d*); 38.8 (*s*); 38.7 (*s*); 36.1 (*t*); 34.1 (*t*); 32.9 (*d*); 32.8 (*t*); 32.1 (*t*); 29.7 (*t*); 29.7 (*q*); 29.0 (*t*); 27.2 (3*q*); 24.6 (*t*); 21.7 (*q*); 18.5 (*q*); 17.7 (*q*). HR-MS: 388.2953 ($C_{25}H_{40}O_3^+$; calc. 388.2977).

Kempa-6,8-dien-3β-yl Pivalate (=*(2a*RS,*3*SR,*4a*SR,*7*RS,*7a*SR,*10b*SR,*10c*SR*)-2,2a,3,4,4a,5,6,7,7a,8,10b,10c-Dodecahydro-2a,7,10,10c-tetramethylnaphth[2,1,8-*cde*]azulen-3-yl 2,2-Dimethylpropanoate*; **42**). Under N_2, Me_3SiCl (12 μl, 90.4 μmol) was added to **41** (8.8 mg, 22.6 μmol) in THF (2 ml) at 0°, and the mixture was stirred at 20° for 27 h. The mixture was diluted with H_2O (10 ml), the aq. phase extracted with AcOEt (3 × 5 ml), the combined org. phase washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 20:1): 8.4 mg (quant.) of **42**. White solid. M.p. not measured. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.68 (br. *d*, *J* = 7.6, H–C(9)); 5.62 (br. *s*, H–C(6)); 5.13 (*dd*, *J* = 7.6, 9.2, H–C(3)); 2.73 (*d*, *J* = 17.7, H_α–C(5)); 2.26 (*d*, *J* = 1.9, H–C(16)); 1.92 (*dd*, *J* = 3.4, 17.4, H_β–C(5)); 1.82 (*s*, Me(19)); 1.20

(*s*, Me_3CCO); 1.00 (*s*, Me(18)); 0.91 (*s*, Me(17)); 0.81 (*d*, $J = 6.4$, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.3 (*s*, C=O); 144.6 (*s*, C(8)); 133.5 (*s*, C(7)); 130.9 (*d*, C(9)); 125.1 (*d*, C(6)); 75.5 (*d*, C(3)); 67.1 (*d*); 55.7 (*d*, C(11)); 45.7 (*s*, C(4)); 40.9 (*t*); 40.0 (*s*, C(15)); 38.9 (*s*, Me_3CCO); 36.7 (*d*); 36.1 (*t*); 32.6 (*t*); 30.7 (*d*); 30.2 (*t*); 29.5 (*q*, C(18)); 27.2 (3*q*, Me_3CCO); 25.7 (*t*, C(10)); 22.6 (*q*, C(19)); 20.6 (*q*, C(20)); 17.2 (*q*, C(17)). HR-MS: 370.2865 ($C_{25}H_{38}O_2^+$; calc. 370.2872).

Kempa-6,8-dien-3β-ol (= *(2a*RS,*3*SR,*4a*SR,*7*RS,*7a*SR,*10b*SR,*10c*SR*)-2,2a,3,4,4a,5,6,7,7a,8,10b,10c-Dodecahydro-2a,7,10,10c-tetramethylnaphth[2,1,8-*cde*]azulen-3-ol*; **4a**). Under N_2, $LiAlH_4$ (2 mg, 52.7 μmol) was added to a stirred soln. of **42** (3.0 mg, 7.72 μmol) in THF (1.5 ml) at r.t., and the mixture was stirred for 30 min at 25°. The mixture was diluted with H_2O (10 ml), the aq. phase extracted with Et_2O (3 × 5 ml), the combined org. phase washed with brine (3 × 5 ml), dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 20:1): 2 mg of **4a**. Colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.68 (br. *d*, $J = 7.0$, H–C(9)); 5.63 (br. *s*, H–C(6)); 4.08 (*m*, H–C(3)); 2.61 (br. *d*, $J = 16.5$, H_α–C(5)); 2.22 (br. *d*, $J = 2.2$, H–C(16)); 1.86 (*dd*, $J = 3.5$, 16.5, H_β–C(5)); 1.82 (*s*, Me(19)); 1.11 (*s*, Me(18)); 0.86 (*s*, Me(17)); 0.81 (*d*, $J = 6.1$, Me(20)). ^{13}C-NMR (125 MHz, $CDCl_3$): 144.8 (*s*, C(8)); 133.7 (*s*, C(7)); 130.7 (*d*, C(9)); 125.1 (*d*, C(6)); 72.6 (*d*, C(3)); 67.2 (*d*); 55.8 (*d*, C(11)); 47.6 (*s*, C(4)); 40.1 (*s*, C(15)); 39.6 (*t*); 37.0 (*d*); 36.1 (*t*); 35.9 (*t*); 30.8 (*d*); 30.4 (*t*); 29.5 (*q*, C(18)); 25.8 (*t*); 22.6 (*q*, C(19)); 20.6 (*q*, C(20)); 17.5 (*q*, C(17)). HR-MS: 286.2297 ($C_{20}H_{30}O^+$; calc. 286.2297).

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Received June 26, 2003