# 102. New Olefinic Cyclizations by Oxymetallation. Conversion of (−)-Elemol to (−)-Selina-4α,11-diol (Cryptomeridiol) and (−)-Guai-1(10)-ene-4α,11-diol

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Dedicated to Professor *André Dreiding* on the occasion of his 60th birthday

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*Summary*

Acetoxythallation of (−)-elemol acetate (**1b**) yields a diacetate **2b** which after treatment with lithium aluminium hydride gives (−)-guai-1(10)-ene-4α,11-diol (**2a**). (−)-Elemol (**1a**) is converted to (−)-selina-4α,11-diol (**9**, cryptomeridiol) by hydroxymercuration followed by reductive demercuration. (+)-γ-Elemene (**5**) similarly yields (+)-selin-7(11)-en-4α-ol (**11**, juniper camphor). The stereochemistry and mechanism of these metal salt-induced olefinic cyclization and their biogenetic implication are discussed.

Oxymetallation is a useful tool for the functionalisation of olefins or other nucleophilic substrates [1]. Thus oxymercuration followed by reductive demercuration represents a simple and convenient procedure for regiospecific (*Markovnikov*-type) hydration of olefins [2]. Oxythallation is another versatile synthetic method for the oxidation of many types of substrates [3]. Lead tetraacetate represents a classical reagent for the functionalisation of alkenes [4]. Electrophilic metal salts, such as those used in oxymetallation reactions, may also be useful reagents for olefinic cyclizations. There are a few interesting reports [5-11] on this subject *(vide infra)* although no systematic investigations have been carried out. Further studies in this field should provide useful synthetic tools for olefinic cyclizations or rearrangements and also give valuable information on the stereochemistry and mechanism of metallation reactions. In this paper we report some new regio- and stereospecific olefinic cyclizations induced by thallium(III) and mercury(II) salts.

**Results.** - Treatment of elemol acetate **1b** with thallium(III) nitrate (TTN) in acetic acid for 20 min at room temperature gave a crude diacetate **2b**, which was treated with lithium aluminium hydride to give the diol **2a** in 63.5%

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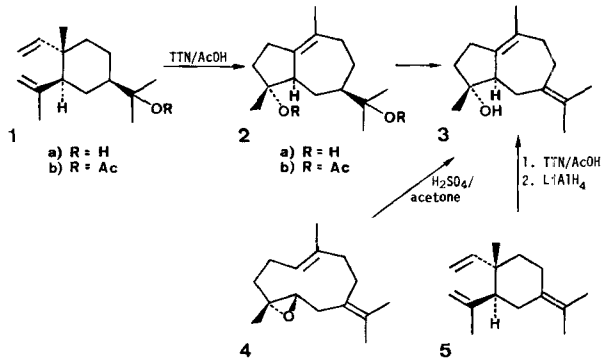
crystalline overall yield. Treatment of elemol (**1a**) with TTN in acetic acid under similar conditions as those used in the TTN reaction of the corresponding acetate yielded a product which, without purification, was treated with lithium aluminium hydride to give the diol **2a**, although in lower yield than in the reaction with elemol acetate.




The structure of diol **2a** followed from its chemical composition and spectral data. The chemical composition $C_{15}H_{26}O_2$ of **2a** was shown by its elemental analysis, mass spectrum ($M^+$ at 238 *m/e*) and from its $^1$H- and $^{13}$C-NMR. spectra (15 C and 24 H bonded to carbon). The $^{13}$C-NMR. spectrum established the bicyclic nature of the compound as well as the presence of the tetrasubstituted double bond, the two quarternary carbon atoms bonding to the hydroxyl groups, the two tertiary, five secondary and four primary (methyl groups) carbon atoms. The $^1$H-NMR. spectrum revealed the presence of the three methyl groups attached to the carbinol carbon atoms and one olefinic methyl group. Further information from the $^1$H-NMR. spectrum could not be obtained due to the complex and unresolved nature of the spectrum. However, a lanthanide induced shift (LIS) study provided additional and conclusive information about the structure and configuration of the diol **2a**.

Addition of Eu(fod)$_3$ induced significant shifts of the signals assigned to $H_\alpha$–C(5), $H_\alpha$–C(6), $H_\beta$–C(6) and $H_\alpha$–C(7) as well as of the three methyl signals due to the protons of the methyl groups on the carbinol carbon atoms. Decoupling experiments firmly established the above assignments. The observed coupling patterns could be accounted for by the steric arrangements shown in *Figure 1*.

The induced shifts exhibit a good linear correlation to the amount of Eu(fod)$_3$ added. Computing the LIS, using the configuration and conformation shown in *Figure 1* gives excellent agreement between observed and calculated shifts *(Table)*. The calculated shifts are obtained by assuming that the shift reagent independently complexes with HO–C(4) and HO–C(11)[1]).

[1]) Similar methods of simulating the LIS of bifunctional compounds have been reported [12]. Mr. *Michael Weber* of the Royal Institute of Technology, Stockholm, Sweden, and Mr. *Antti Talvitie,* University of Jyväskylä, Jyväskylä, Finland, are gratefully acknowledged for computation of the LIS.

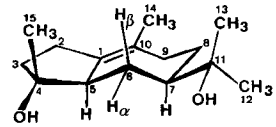


Fig. 1. *Stereostructure of (−)-guai-1(10)-ene-4α,11-diol* (**2a**)

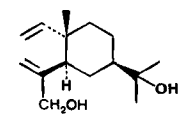
Table. *Observed and calculated Eu(fod)$_3$-induced proton chemical shifts* (*Δ*Eu-values) *and observed coupling constants of the diol* **2a**

| Proton No[a]) | *Δ*Eu-values[b]) | | Coupling constants[c]) (assignments) |
|---|---|---|---|
| | Observed | Calculated | |
| H–C(5) | 9.16 | 9.72 | *d;* 11(5,6β), ≃0(5,6α) |
| $H_α$–C(6) | 11.75 | 11.79 | *d;* 12(6α,6β), ≃0(6α,5 and 6α,7) |
| $H_β$–C(6) | 6.33 | 5.82 | *qa;* 12(6β,6α), 11(6β,5), 10(6β,7) |
| H–C(7) | 8.21 | 8.75 | *t;* 10(7,6β and 7,8β), ≃0(7,6α and 7,8α) |
| 3 H–C(12) | 6.00 | 7.88 | *s* |
| 3 H–C(13) | 5.97 | 5.18 | *s* |
| 3 H–C(15) | 5.85 | 7.65 | *s* |
| 3 H–C(14) | 1.43 | 2.06 | *s* |

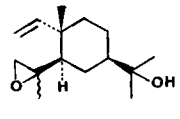
[a]) For proton numbering see the stereostructure of **2a** in *Figure 1.*
[b]) *Δ*Eu-values are given in ppm.
[c]) Coupling constants *(J)* are given in Hz. For abbreviations see Experimental Part, general section.

The structure of the diol **2a** was confirmed by a chemical correlation with a compound of known structure. A partial dehydration of the diol with FILTROL in dry dioxane yielded a complex mixture with the alcohol **3** as one of the main constituents. This alcohol was isolated by chromatography on a silver nitrate impregnated support, but could not be induced to crystallize. However, its IR. and NMR. spectra were superimposable on those of guaia-1(10),7(11)-dien-4α-ol (**3**) previously prepared by cyclization of 4,5-epoxygermacra-1(10),7(11)-diene (**4**) [13]. The alcohol **3** was also obtained in low yield (24%) by a TTN treatment of (+)-γ-elemene (**5**) in acetic acid followed by a treatment of the crude reaction mixture with lithium aluminium hydride.

In our attempts to confirm the structure of the diol **2a** by an independent chemical correlation we tried to perform a cationic cyclization of the allylic



**6**



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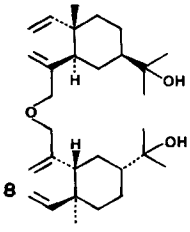
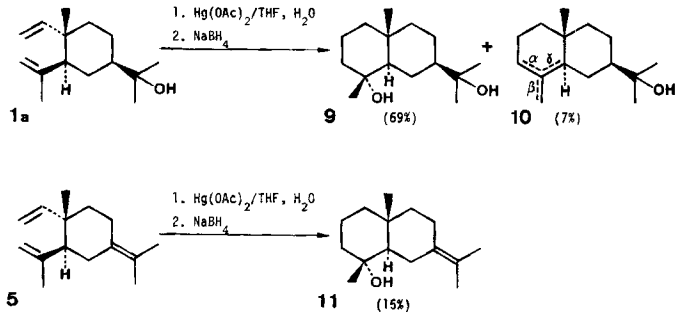
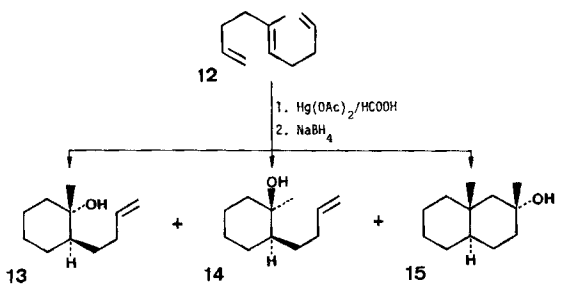


**8**

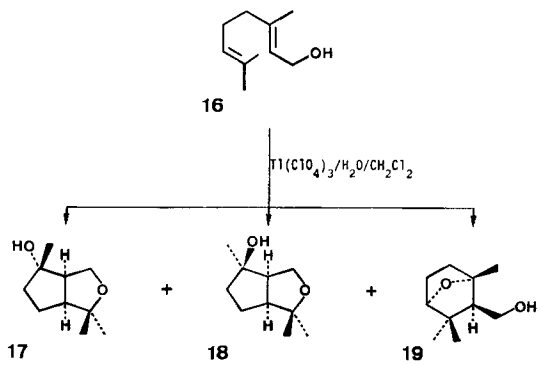



alcohol **6**. This alcohol is readily obtained by a base-induced ring opening of elemol 3,4-epoxide **7**. Various solvolytic conditions were tested but no cyclization product could be detected. Instead the dimeric ether **8** was obtained. This ether was also obtained as the main product in our attempts to prepare the *p*-toluenesulfonyl ester of the allylic alcohol by standard procedure using *p*-toluenesulfonyl chloride in pyridine.

In order to gain further information about the metal salt-induced olefinic cyclization of elemol (**1a**) the oxymetallation was performed with mercury(II) acetate in aqueous alcohol followed by reductive demercuration with potassium borohydride following the usual procedure [2] employed for *'Markovnikov'*-hydration of olefins. The crystalline diol **9** thus obtained in good yield (69%) was identical with (−)-selina-4$\alpha$,11-diol (cryptomeridiol) [14]. Small amounts of $\alpha$-, $\beta$- and $\gamma$-eudesmols (**10**) were also formed. Similar treatment of (+)-$\gamma$-elemene (**5**) gave (+)-selin-7(11)-en-4$\alpha$-ol (**11**, juniper camphor) [15] [16] although in lower yield (about 15%).

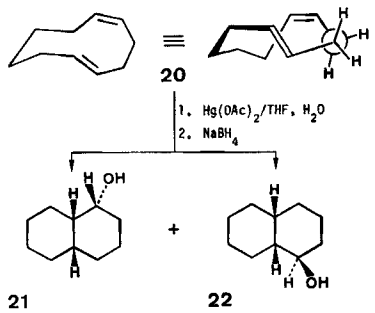



**Discussion.** – Oxymetallation reactions are generally believed to proceed *via* a cationic organometallic $\pi$-complex, which reacts further with nucleophiles. If the latter is a double bond within the same molecule, an olefinic cyclization occurs. Such a process may proceed in a stepwise manner or be concerted. A few such olefinic cyclizations are reported. Thus 5-methyldeca-1,5*E*,9-triene (**12**) in formic acid reacts with mercury(II) acetate. The alcohols **13** to **15** were isolated after reductive demercuration with sodium borohydride [7]. These alcohols were obtained in slightly different proportions depending on the reaction conditions (temperature and time). Similar cyclizations have been carried out with other polyenes [5–8].



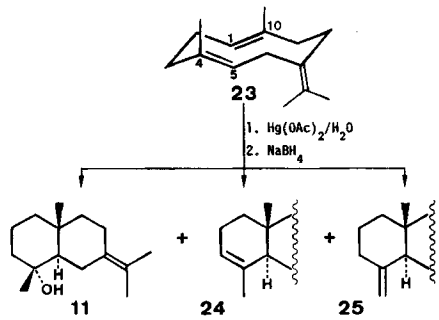

Recently a cyclization of geraniol (**16**) with thallium(III) perchlorate has been shown to give the bicyclic hydroxy ethers **17** to **19** [10].

A transannular olefinic cyclization has been observed in the reaction of 1*Z*,5*E*-cyclodecadiene (**20**) with mercury(II) acetate [9]. Reductive demercuration of the reaction product thus obtained gave *cis,cis*-1-decalol (**21**). A small amount of the *cis,trans*-1-decalol (**22**) was also formed. The formation of the main product (**21**) was rationalized by attack of the electrophilic mercury(II) ion on the *E*-double bond and binding of the nucleophile at the *Z*-linkage. An attack of the metal ion at the *Z*-linkage and the nucleophile at the *E*-double bond account for the formation of the minor product (**22**).




Transannular cyclization has also been observed in the reaction of 1(10),4,7(11)-germacratriene (**23**) with mercury(II)acetate under the standard conditions of olefin hydration [11]. In this reaction (+)-selin-7(11)-en-4$\alpha$-ol (**11**) was obtained together with small amounts of the dienes **24** and **25**. This cyclization was explained [11] by reaction in a crown conformation with preference for an attack of the electrophilic mercury(II) ion at the 1,10-bond. A concerted mechanism with carbon-electrophile and carbon-carbon bond formation was preferred for this reaction. A 'cyclization product-like' transition state was suggested to be involved in the rate-determining step of the reaction.

The olefinic cyclizations of elemol (**1a**) or its acetate (**1b**) with mercury(II) acetate and thallium(III) nitrate, which now have been revealed, provide evidence for a mechanism with carbon-metal and carbon-carbon bond formation occurring




synchronously. A significant fact, which supports such a mechanism, is that epoxidation of elemol occurs at the 3,4-position and that metallation with mercury(II) acetate is also expected [2b] on that position. The observed reaction must involve metallation at the 1,2-double bond with an *anti-Markovnikov* nucleophilic attack at the primary 2-position resulting in a carbon-metal bond at C(1). The cyclization of elemol thus should proceed *via* a rate-determining product-like transition state [11] followed by bonding of the nucleophile from a *pseudo*-equatorial direction as indicated in the stereo-formula **26**. This fully accounts for the stereo-specificity of the reaction. The intermediate organometallic species **27a** of the oxymercuration reaction is then reduced to yield cryptomeridiol (**9**). The thallium(III) ligand of the intermediate organometallic species **27b** of the acetoxy-thallation reaction is a very good leaving group [3]. Therefore, a rearrangement occurs which is analogous to that observed in the solvolysis of the *O*(1)-tosylate of selin-7(11)-ene, 1$\beta$-4$\alpha$-diol [13].

Our experiments provide additional support for the fact that electrophilic metal salts are excellent reagents for regio- and stereospecific cyclization reactions and cationic rearrangements. Further systematic studies will reveal rules for the best choice of metal salts and reaction conditions.

It is not inconceivable that the rearrangements described possess some biogenetic relevance. It is striking that compounds of the elemane, eudesmane, guaiane and germacrane group are often congeneric in the plant [17]. In these cases germacrane-type sesquiterpenes are believed to function as common precursors [18–20]. So far the elemenes have only been regarded as end products or

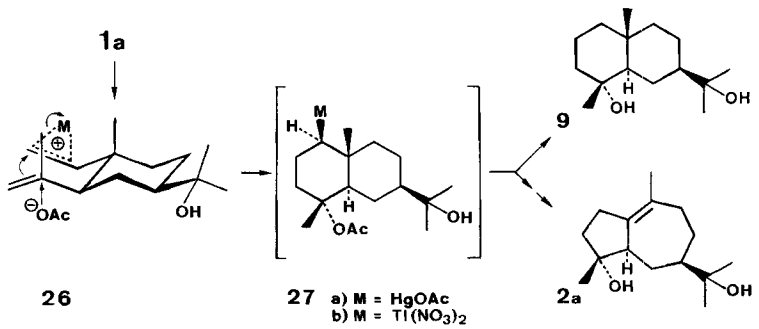



Fig. 2. *Pathway of oxymetallation reactions of* (–)-*elemol* (**1a**)

intermediates in biogenetic-type rearrangements [19] [21]. On the basis of the cyclization reactions of (−)-elemol (**1a**) described in this work *(Fig. 2)* elemol derivatives should also be considered as possible key precursors, in particular in the biotransformation of the elemenes into derivatives of the guaiane group. The *in vitro* reaction sequence of elemol outlined in *Figure 2*, may also take place in the plant as a metal catalyzed, enzymatic oxycyclization reaction.

Part of this work was performed during a stay by one of us *(T.N.)* as a visiting professor of the *Firmenich SA*. *T.N.* expresses his sincere thanks to Dr. *Roger Firmenich* and to all the collaborators of *Firmenich SA* for this stimulating visit. A travel grant from the *Swedish National Science Research Council* (NFR K 2621-011) is gratefully acknowledged. The authors thank Mr. *W. Giersch*, Mr. *Ch. Vial*, Mrs. *Beatrice Frey* and Mr. *A. Hauser* for skilful technical assistance and Mr. *W. Thommen* for carrying out the $^{13}C$- and shift reagent experiments. Professor *J.K. Sutherland*, the University of Manchester, England, is gratefully acknowledged for IR. and NMR. spectra of guaia-1(10),7(11)-dien-4*a*-ol.

## Experimental Part

*General.* Melting points are uncorrected. – IR. spectra were recorded by means of *Perkin Elmer* A 21 and 720 spectrometers (bands are given in $cm^{-1}$). – NMR. spectra were measured on *Varian* A-60 (60 MHz) and *Bruker* HFX-90 (90 MHz) instruments in $CCl_4$ or $CDCl_3$. Chemical shifts ($\delta$) are given in ppm relative to TMS (internal standard). Coupling constants are in Hz and multiplicities are as follows: *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quartet, *m* = multiplet, br. = broad, u. = the peak position is uncertain. Mass spectra (MS.) were determined on an *Atlas* CH4 instrument, electron energy: 70 eV. Results are quoted as *m/e* (% most abundant fragment), and generally, the ten most important fragments are quoted. For chromatography on silica gel, hexane containing increasing amounts of ether was employed.

1. *Oxythallation of (−)-elemol acetate* (**1b**). (−)-Elemol (**1a**, m.p. 50–51.5°, $[\alpha]_D^{20} - 3°$ (*c* = 6%, $CHCl_3$)), was acetylated with excess acetic anhydride in dry pyridine. After usual work-up the acetate **1b** was purified by distillation (b.p. 155–160°/8 Torr), $[\alpha]_D^{20} = -1°$ (*c* = 2%, $CHCl_3$) [22].

A solution of 4.4 g of thallium(III) nitrate (TTN), $Tl(NO_3)_3 \cdot 3\,H_2O$, in 15 ml of acetic acid was slowly added (20 min) with stirring to a solution of 1.32 g of the acetate **1b** in 5 ml of acetic acid at *ca.* 10°. The reaction mixture was kept at RT. for 10 min, then filtered through *Celite* with hexane, to remove the inorganic residue. The solution was washed with water, aqueous $NaHCO_3$-solution, brine and finally water. The solvent was evaporated yielding an oil (1.5 g) which, without further purification, was dissolved in 20 ml of dry ether and reduced with 0.5 g of $LiAlH_4$ in 20 ml of ether. The excess reagent was decomposed with moist $Na_2SO_4 \cdot 10\,H_2O$ and the product isolated by filtration and concentration. The crude product partly crystallized. Recrystallization from chloroform/light petroleum (b.p. 40–60°) yielded 0.65 g of (−)-guai-1(10)-ene-4*a*,11-diol (**2a**). A further 0.15 g of the diol **2a** was obtained by chromatography of the mother liquors on silica gel in ether/hexane. Yield: 0.8 g (63.5%), m.p. 116–117°, $[\alpha]_D^{20} = -31.8°$ (*c* = 0.94%, $CHCl_3$). – IR. (KBr): 3320, 1630 (weak), 1460, 1435, 1380, 1370, 1360, 1315, 1300, 1225, 1180, 1150, 1135, 1115, 1100, 1065, 1055, 980, 940, 905, 830. – $^1H$-NMR. ($CDCl_3$): 1.17 (*s*, 3 H); 1.19 (*s*, 6 H); 1.66 (*s*, 3 H). – LIS-NMR.: see *Table*. – $^{13}C$-NMR. (15% in $CDCl_3$): 138.2 and 129.8 (*s*, C(1) and C(10)); 81.0 and 73.5 (*s*, C(4) and C(11)); 54.5 and 53.1 (*d*, C(5) and C(7)); 39.9, 34.7, 29.1, 27.5, and 26.9 (*t*, C(2), C(3), C(6), C(8), and C(9)); 28.9, 27.7, 23.0, and 21.8 (*qa*, C(12), C(13), C(14), and C(15)). – MS.: 93 (100), 43 (83), 162 (60), 59 (54), 119 (48), 82 (46), 41 (38), 67 (32), 28 (31), 159 and 105 (30) ... 205 (24), 220 (23), 238 (1, $M^+$).

$C_{15}H_{26}O_2$ (238.36) Calc. C 75.58 H 11.00% Found C 75.64 H 11.03%

2. *Partial dehydration of (−)-guai-1(10)-ene-4a,11-diol* (**2a**). To a solution of 0.5 g of **2a** in 20 ml dioxane was added 0.05 g of FILTROL (Grade 13; Filtrol Corporation, Vernon, Calif., USA) and the mixture was heated under reflux for 4 h. The dehydration was followed by GC. (15% Carbowax 20 M, 1 m, 230°; rel. retention times of starting material and main product, 1.00 and 0.35 respectively).

After cooling, the reaction mixture was poured into ice/water and extracted with a mixture of hexane and ether. The combined organic extracts were washed with aqueous $NaHCO_3$-solution and water. Evaporation of the solvents yielded 0.4 g of an oil which was chromatographed on silica gel (15 g). Hexane/ether 8:2 eluted 0.2 g of an oily mixture of dienols of which guaia-1(10),7(11)-dien-4$\alpha$-ol (**3**) was one of the main constituents (GC., TLC., IR., NMR.). This alcohol was purified by re-chromatography on silver nitrate-impregnated silica gel (20% $AgNO_3$), from which 0.025 g were eluted after some minor impurities by hexane/ether 8:2. The spectra (IR. and NMR.) were superimposable on those of an authentic sample of **3** [13].

3. *Oxythallation of* (+)-$\gamma$-*elemene* (**5**). A solution of 1.02 g of **5**, prepared by dehydration of (−)-elemol (**1a**) [22], in 5 ml acetic acid was treated with 4.4 g of TTN in 15 ml of acetic acid and the oily reaction product (1.4 g) reduced with $LiAlH_4$ as described in 1. The crude product was chromatographed on 15 g of silica gel. After a complex non-polar fraction, hexane/ether 8:2 eluted an alcohol fraction (0.26 g, yield 24%) which on rechromatography on silver nitrate-impregnated silica gel (20% $AgNO_3$) yielded a fraction with spectral (IR., NMR.) and chromatographic (TLC. and GC.) properties similar to those of guaia-1(10)-7,11-dien-4$\alpha$-ol (**3**) [13] (*cf.* sect. 2). This oily fraction could not be induced to crystallize.

4. *Oxymercuration-demercuration of elemol* (**1a**) (*cf.* [2a]). A solution of 2.2 g of elemol (**1a**) in 10 ml tetrahydrofuran (THF) was slowly added to a stirred solution of 3.5 g of $Hg(OAc)_2$ in 10 ml of water and 10 ml of THF. After 30 min at RT. 10 ml of 3.0N NaOH was added followed by 10 ml of a solution of 0.2 g of sodium borohydride in 3.0N NaOH. Mercury settled, and the organic layer was separated and washed with water. Evaporation of the solvents yielded 2.1 g of a colourless oil which crystallized upon standing. Recrystallization from ether in light petroleum (b.p. 40–60°) yielded 1.35 g of (−)-selina-4$\alpha$,11-diol (**9**, cryptomeridiol), m.p. 134–136° [14] (m.p., mixed m.p., IR., NMR. and MS.). The crude materials (0.6 g) from the combined mother liquors were chromatographed on silica gel (20 g), from which hexane/ether 9:1 eluted a partly crystalline fraction (0.15 g), which was a mixture of $\alpha$-, $\beta$-, and $\gamma$-eudesmol (**10**) by comparison (TLC., GC., IR., and NMR.) with an authentic sample. Ether/hexane 1:1 eluted further amounts (0.3 g) of the diol. Total yield: 1.65 g (69%). – IR. (KBr): 3300, 1460, 1380, 1360, 1335, 1295, 1260, 1180, 1120, 1090, 1060, 1020, 990, 945, 920, 910, 875, 855, 805, 780. – $^1$H-NMR. ($CDCl_3$): 0.88 (*s*, 3 H); 1.12 (*s*, 3 H); 1.20 (*s*, 6 H); 0.9–2.2 (several *m*, 14 H). – MS.: 59 (100), 43 (80), 149 (55), 41 (41), 81 (38), 109 (32), 93 and 71 (30), 55 (29), 95 (26), 67 (24) ... 164 (21), 182 (3), 189 (17), 204 (9), 222 and 225 (1), 240 (0, $M^+$).

5. *Oxymercuration-demercuration of* (+)-$\gamma$-*elemene* (**5**) was carried out on 1.02 g (5 mmol) of **5** as described in 4. The oily product (1.1 g) was chromatographed on 20 g of silica gel. Hexane/ether 9:1 eluted a fraction which crystallized. Recrystallization from methanol afforded 0.15 g (14%) of (+)-selin-7(11)-en-4$\alpha$-ol (**11**, juniper camphor), m.p. 162–165°, $[\alpha]_D^{20} = \pm 0°$, ($c = 0.8\%$, $CHCl_3$) [15] [16] (m.p., mixed m.p., GC., TLC., IR., NMR. and MS.). – $^1$H-NMR. ($CDCl_3$): 0.98 (*s*, 3 H); 1.15 (*s*, 3 H); 1.78 (br. *s*, 6 H); 0.8–2.0 (several *m*, approx. 10 H); 2.0–2.8 (2 u. *m*, 2 H); 2.85 (br. *d*, $J = 12$, 1 H, $H_\beta$–C(6)). – MS.: 28 (100), 107 (70), 43 (67), 77 (57), 79 (56), 108 (53), 189 (52), 44 and 204 (43), 41 (41), 121 (38), 81 and 161 (34) ... 222 (25, $M^+$).

6. *Preparation of the allylic alcohol* **6**. Elemol 3,4-epoxide (**7**, mixture of two diastereoisomers) was prepared by epoxidation of (−)-elemol acetate (**1b**), as described for $\gamma$-elemene [23], followed by saponification of the resulting epoxy acetate in methanolic NaOH. A solution of 2.38 g of **7** in 10 ml of dry ether was slowly added to a solution of lithium diethylamide (prepared by adding 9.3 g of a 15% solution of butyl lithium in hexane slowly to a solution of 1.6 g of diethylamine in 5 ml of dry ether). The reaction mixture was heated under reflux for 48 h ($N_2$-atmosphere) and poured into ice/water. The organic phase was washed with aqueous sulfuric acid, aqueous $NaHCO_3$-solution, water and dried ($Na_2SO_4$). Evaporation yielded an oil, which crystallized on standing. Recrystallization from ether in light petroleum (b.p. 40–60°) yielded 1.0 g of the allylic alcohol **6**. The combined mother liquors (1.6 g) were chromatographed on silica gel (20 g). Ether eluted a further 0.5 g of **6**. Total yield: 1.5 g (63%), m.p. 75–76°, $[\alpha]_D^{20} = -21°$ ($c = 8.2\%$, $CHCl_3$). – IR.: 3350, 3090, 1820, 1720, 1660, 1640, 1440, 1415, 1380, 1365, 1235, 1180, 1065, 1040, 1005, 955, 940, 910, 895, 885, 850, 805, 780, 740. – $^1$H-NMR. ($CCl_4$): 0.92, 1.10 and 1.12 (*s*, 3 H each, 3 $CH_3$); 0.8 to 2.3 (br. u. *m*, 8 H); 3.87 (br. *s*, 2 H, O–$CH_2$); 4.72, 4.90 and 5.05 (*m*, 4 H, 2 =$CH_2$); 5.72 (*d*×*d*, $J = 10$ and 18, 1 H, C*H*=$CH_2$). – MS.: 59 (100), 93 (80), 43 (72), 41 (56), 81 (45), 79 (42), 67 (39), 55 (37), 107 (36), 69, 91 and 121 (31) ... 177 (16), 187 (5), 189 (14), 202 (2), 205 (4), 220 (3), 238 (0, $M^+$).

$C_{15}H_{26}O_2$ (238.36) Calc. C 75.58 H 11.00% Found C 75.35 H 10.49%

7. *Solvolysis of the allylic alcohol* **6**. A solution of 0.24 g of **6** and 0.05 g of oxalic acid in 5 ml of acetic acid was stirred at 80° for 20 h, then poured into ice/water and extracted with ether. The ethereal solution was washed (water, $NaHCO_3$) and dried ($Na_2SO_4$). The solvent was evaporated, and the residue was chromatographed on silica gel (10 g). Ether/hexane 1:1 eluted the main product (0.15 g (54%), TLC., ether, Rf = 0.37). Small amounts of a crystalline compound, m.p. 50–51° (TLC., ether, Rf = 0.56), identical (m.p., mixed m.p., IR., NMR.) with the dimeric ether **8** (below, in sect. 8), were also isolated. The main product was the allylic monoacetate of the starting material. – IR. (film): 3450, 3080, 1820, 1730, 1640, 1465, 1440, 1415, 1370, 1230, 1120, 1085, 1005, 960, 910, 850, 800, 780, 770, 740. – $^1$H-NMR. ($CCl_4$): 0.98 (*s*, 3 H, $CH_3$); 1.14 (*s*, 6 H, 2 $CH_3$); 0.85 to 2.1 (several br. u. *m*, 8 H); 2.03 (*s*, 3 H, $COCH_3$); 4.38 (br. *s*, 2 H, O–$CH_2$); 4.68 to 5.18 (several *m*, 4 H, 2 =$CH_2$); 5.74 (*d*×*d*, *J* = 10 and 18, 1 H, C*H*=$CH_2$).

8. *Attempted preparation of the* p-*toluenesulfonate of the allylic alcohol* **6**. *p*-Toluenesulfonyl chloride (0.85 g) and 0.95 g of the allylic alcohol **6** in 10 ml of pyridine were stirred for 15 h at RT., then poured into ice/water and extracted with ether. The ether extract was washed (aqueous sulfuric acid, water), dried ($Na_2SO_4$) and concentrated to yield an oil (1.0 g) which was chromatographed on silica gel (15 g). Ether/hexane eluted 0.35 g (38%) of the main product (TLC., ether, Rf = 0.56) which was the dimeric ether **8**; m.p. 50–51° (IR., NMR., MS.). – IR. (film): 3350, 3080, 1820, 1640, 1465, 1440, 1410, 1375, 1295, 1255, 1155, 1135, 1115, 1085, 1055, 1010, 960, 910, 845, 800, 770, 750. – $^1$H-NMR. ($CCl_4$): 0.95 (*s*, 6 H, 2 $CH_3$); 1.15 (*s*, 12 H, 4 $CH_3$); 1.0 to 2.4 (several br. u. *m*, 16 H); 3.90 and 4.00 (*AB*-spectrum, $J_{AB}$ = 12, each 2 H, 2 O–$CH_2$); 4.65 to 5.25 (several *m*, 8 H, 4 =$CH_2$); 5.75 (*d*×*d*, *J* = 10 and 18, 2 H, 2 C*H*=$CH_2$). – MS.: 59 (100), 93 (48), 43 (36), 41 (31), 81 (27), 107 (24), 79 (23), 91 (20), 67 (19), 105 (17) ... 159 (8), 162 (5), 169 (1), 187 (1), 189 (2), 195 (4), 209 (3), 223 (1), 238 (< 1), 252 (< 1), 458 (0, $M^+$).

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