# An Unexpected (3 → 2)-Hydride Shift in Phyllocladane (= 13β-Kaurane) Diterpenoids and in Related Trimethyl-Substituted Bi- and Tricyclic Compounds

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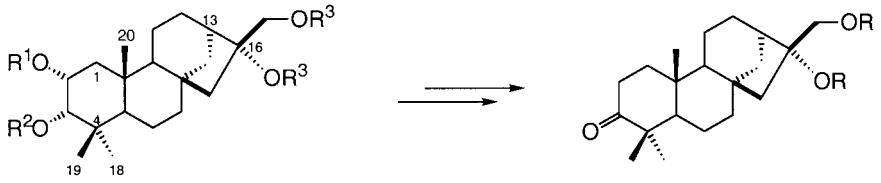
The conversion of 2α,3α-dioxy-substituted phyllocladane derivatives into the corresponding 3-ketone proceeds in an unexpected manner: Depending on the reaction conditions, the corresponding 3β-hydroxy-substituted compound is formed almost quantitatively, or the desired ketone can be isolated directly (see preceding paper). The reaction mechanism is now disclosed to be a stereospecific C(3) → C(2)-hydride shift by investigating the reactions of the synthesized (±)-*trans*-decalin-type (*trans*-1,5,5-trimethylbicyclo[4.4.0]decanes) and (±)-podocarpane-type (*trans*-1,2,3,4,4a,9,10,10a-octahydro-1,1,4a-trimethylphenanthrenes) model compounds **25** and **35** and of their D-labeled isomers **25′** and **35′** (*Scheme 6*). The latter afforded the corresponding 3β-hydroxy (2β-D)-derivatives **38** and **39** as well as the (2β-D)-3-ketones of the general type **5b′** (*e.g.*, **36′**), thus evidencing a suprafacial (C3) → C(2)-deuteride shift. This reaction mechanism seems to be a general feature of such 3α,4α-dioxy-substituted 1,5,5-trimethylbicyclo[4.4.0]decane congeners.

**1. Introduction.** – In the preceding paper [1], we reported that the attempted chemical transformation of the natural phyllocladane **1** into the 3-oxo derivative **5a** (calliterpenone; *Scheme 1*) yielded exclusively the 3β-hydroxy derivative **6** when the 2α,3α-diol 2-tosylate **3** was treated with $LiAlH_4$ (*Scheme 2*). Although the favorable conformations of **3** meet neither the steric nor the stereoelectronic requirements, this unexpected reaction was *a priori* considered to proceed *via* an elimination, yielding an enol(ate) and stereospecific reduction of the corresponding ketone **5b** [1]. This hypothesis was strongly supported by the observation that **3** reacts with $LiAlD_4$ to generate exclusively the 3α-deutero compound **6′**[1]). However, closer investigation of

*Scheme 1*

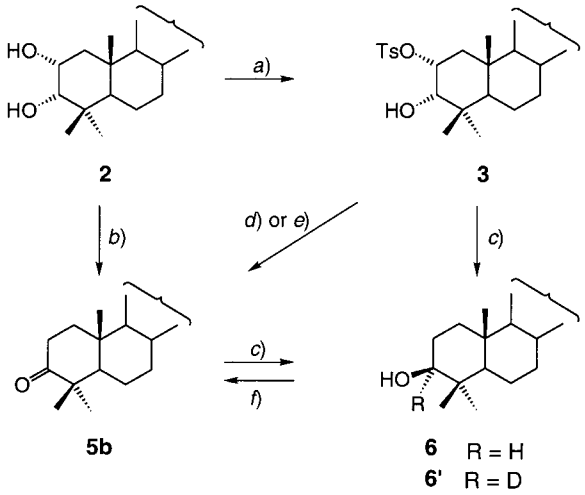



**1** $R^1$ = COCH=C(Me)$_2$, $R^2$ = COMe, $R^3$ = H
**2** $R^1$ = $R^2$ = H, $R^3$ = $Me_2C$
**3** $R^1$ = Ts, $R^2$ = H, $R^3$ = $Me_2C$
**4** $R^1$ = $R^2$ = Ms, $R^3$ = $Me_2C$

**5a** R = H
**b** R = $Me_2C$

[1]) The D-labeled isomers are characterized by a prime (′) added to the number of the corresponding unlabeled isomer.

*Scheme 2*

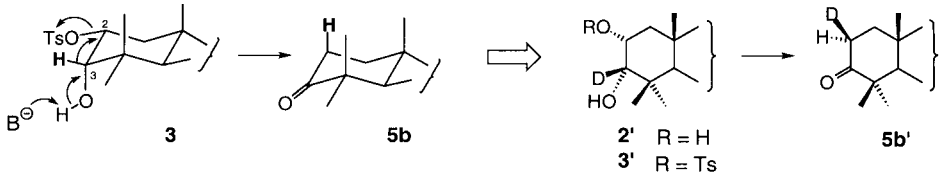



*a*) TsCl, pyridine, r.t.; 94%. *b*) TsCl, pyridine, Δ; 50% (+47% of starting **2**). *c*) $LiAlH_4$ or $LiAlD_4$, THF, r.t.; **6** (90%), **6′** (92%) [1]. *d*) Pyridine or toluene, Δ; 89 and 98%, resp. *e*) NaOEt or NaH, r.t.; 52 and 49%, resp. *f*) PCC, NaOAc, $CH_2Cl_2$, r.t.; 95%.

this reaction (see *Exper. Part*) precluded the formation of an intermediate enol since reaction of **3** with $LiAlH_4$ or $LiAlD_4$ in ($D_4$)THF and workup with $D_2O$ yielded only **6**, and no trace of the expected D–C(2) was observed. But, surprisingly, ketone **5b** could be obtained directly when the 2α,3α-diol **2** was refluxed in pyridine in the presence of *p*-toluenesulfonyl chloride (TsCl) or by heating the neat tosylate **3** in pyridine or toluene (*Scheme 2*). As a consequence, $LiAlH_4$ was assumed to promote the key step of the reaction as a base, rather than being a reducing agent. This could be demonstrated by the successful transformation of the tosylate **3** by NaOEt or NaH, which yielded also **5b** (*Scheme 2*). In addition, refluxing the bis-methanesulfonate derivative **4** in pyridine or toluene left the starting material unchanged, and treatment of **4** with NaOEt or NaH afforded diol **2** by hydrolysis, whereas reaction of **4** with $LiAlH_4$ was known [1] to yield mainly the corresponding 2β-hydroxy compound. These experimental results lead to the formulation of a reaction mechanism for the key step in terms of a suprafacial C(3) → C(2)-hydride shift/elimination process as depicted in *Scheme 3*.

To verify these assumptions, the reaction pathway was tracked by the (3β-D)-isomers of the general type **2′** and **3′** (*Scheme 3*). In the following, we report the syntheses and reactions of **2′** and **3′** and of their (±)-*trans*-decalin-type (*trans*-1,5,5-

*Scheme 3*



trimethylbicyclo[4.4.0]decanes) and (±)-podocarpane-type (*trans*-1,2,3,4,4a,9,10,10a-octahydro-1,1,4a-trimethylphenanthrenes) congeners **25**, **25′**, **35**, and **35′**[2]).

**2. Results and Discusssion.** – 2.1. *Attempted Partial Syntheses of the (3β-D)Phyllocladanes* **2′** *and* **3′** (*Scheme 4*). Reaction of **3** and **5b** with $LiAlH_4$ or $LiAlD_4$ yielded the 3β-hydroxy compounds **6** and **6′** [1], which were mesylated (→ **7** and **7′**) and afforded the olefins **8** and **8′** after forced elimination [2] from the unfavorable conformation. Every attempt to hydroxylate the phylloclad-2-ene **8** by the current methods (*e.g.*, $OsO_4$ and modifications [3], $KMnO_4$, *etc.*) failed, although there are several reports of successful similar transformations [4][3]).

Aiming at the stereospecific reduction of the C(3)-carbonyl group, the 16,17-acetonide **9** of the natural product [1] was then studied. According to reports on similar compounds [4d][6], a significant proportion of the 3α-hydroxy compound should be formed[4]), although the 3β-alcohol is *a priori* expected to be the predominant reduction product. However, all attempts to prepare the 3α-alcohol **10** failed as the attack of the reducing agents exclusively took place from the sterically less-hindered 'α-side', and only the undesired 3β-hydroxy isomers **11**, **11′**, **12**, and **12′** could be obtained, the latter two being the products of acyl migration (see also [6d]). A drawback that precluded many promising combinations of complexing and (chiral) reducing reagents is the lability of both the 2α-oxy-3-oxo and the 16,17-acetonide moieties, and the limited amount of natural material particularly prevented an extensive search for the optimal reaction conditions. Moreover, all efforts to achieve the obvious inversion of the configuration at C(3) in **11** and **11′** by standard $S_N2$ procedures or their modifications (*e.g.*, *Mitsunobu* reaction) also failed. Due to the diequatorial subsitution, ring A adopts the strongly favored chair conformation that renders C(3) inaccessible for a nucleophilic attack.

Although the olefin **8** could not be hydroxylated, it underwent epoxidation either with 3-chloroperbenzoic acid (MCPBA) or dimethyldioxirane [7] to afford exclusively the 2α,3α-epoxides **14** and **14′**, a specificity that was verified by the targeted preparation of the 2β,3β-diastereoisomer **15** (*Scheme 4*). However, all attempts to open **14** and **14′** and the following reactions (see later) again did not afford the desired 2α,3α-dihydroxy compounds.

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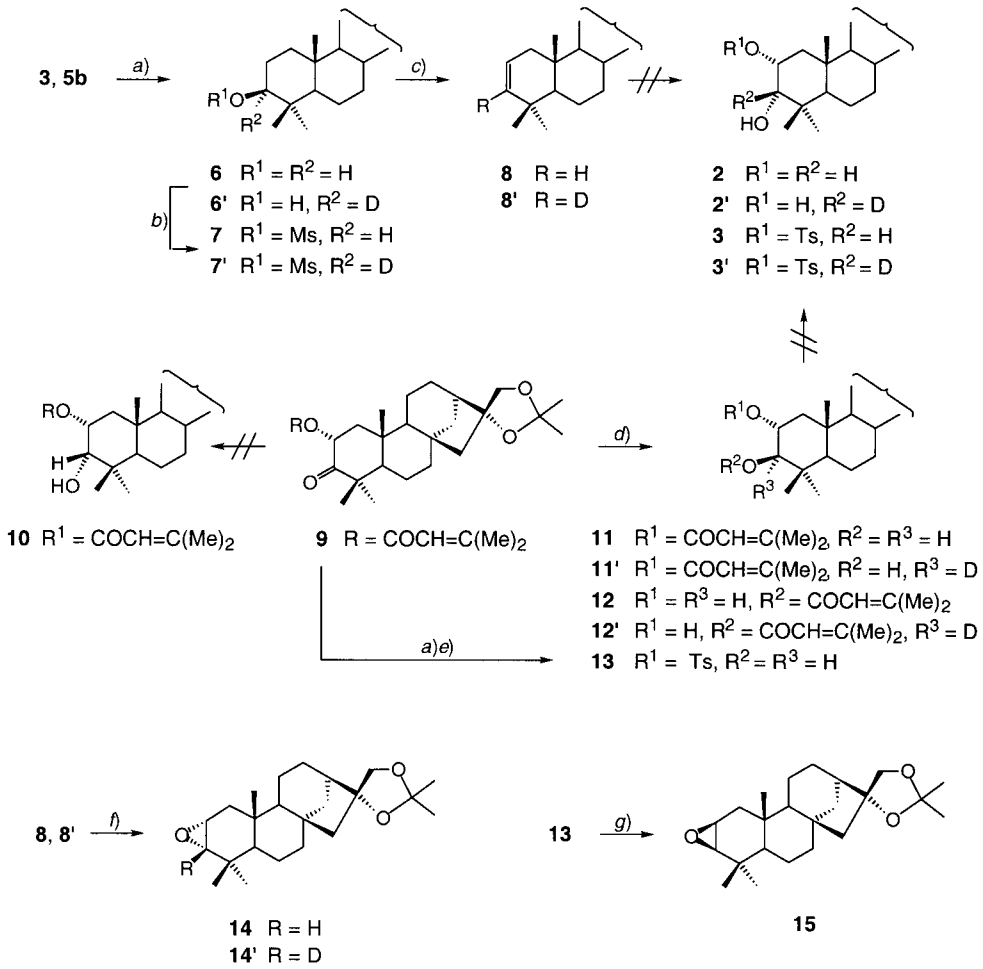
[2]) As all model compounds were prepared as racemates, their structural formulae represent the relative configurations.

[3]) Because the amounts of the natural phyllocladanes were limited, the hydroxylation reactions were also studied with triterpenoid model compounds, as exemplified in [4a–c]. Derived from the commercially available dipterocarpol and betulin, ring-A,B,C analogues of phylloclad-2-ene were prepared. However, in our hands, all experiments to obtain a 2α,3α-diol failed as the 4,4,10-trimethyl-substituted olefins were completely inert in most cases. This failure might be explained by the fact that we used small amounts (< 50 mg), whereas the successful authors were dealing with gram quantities of both starting materials and reagents. Moreover, the yields – if reported – are low and vary from only 3.8% [4d] to a maximum of 36% [4f]. In contrast, we easily obtained 5α-cholestane-2α,3α-diol in quantitative yield when transforming 5α-cholest-2-ene (see [5]).

[4]) Reduction of a 2α-oxy-3-oxo triterpenoids by $NaBH_4$ [6] or 2α-oxy-3-oxo-*ent*-beyerenes by $LiAlH_4$ [4d] afforded the corresponding 3α-alcohols as minor compounds (10% [6a], 13% [6d], 28% [4d]). Surprisingly, they are also reported to be the main products (68% [6c], 84% [6b]). However, applying the reaction conditions of [6b] gave no trace of the desired 3α-alcohol **10**.

*Scheme 4*




*a*) $LiAlH_4$ or $LiAlD_4$, THF, r.t.; **6** (95%), **6′** (99%) [1]. *b*) $MeSO_2Cl$, pyridine, r.t.; **7** (94%), **7′** (84%). *c*) LiBr, $Li_2CO_3$, DMF, 180°; **8** (86%), **8′** (92%). *d*) $NaBH_4$ or $NaBD_4$, THF, r.t.; **11** (51%), **11′** (52%), **12** (24%), **12′** (24%). *e*) TsCl, pyridine, r.t.; 16%. *f*) 0.1M dimethyldioxirane, $Ch_2Cl_2$, −30°; 36%. *g*) $LiAlH_4$, THF, r.t.; 68%.

2.2. *Syntheses of Model Analogues: (±)*-trans-*Decalins* **25** and **25′** *and (±)-Podocarpanes*[2]) **35** *and* **35′**. We were not able to prepare the required (3*β*-D)-phyllocladan-3*α*-ol derivatives **2′** and **3′**. The key problem seems to be the 4,4,10-trimethyl substitution pattern in ring A and the rigidity of the tetracyclic diterpenoid skeleton [1]. Therefore, the closely related model compounds **25**, **25′**, **35**, and **35′** were prepared (*Scheme 5*) to draw the mechanistic conclusions from their reaction behavior with respect to the natural products. Prior to the D-labeled isomers **17′**–**35′**, the respective unlabeled isomers **17**–**35** were characterized, and the synthesis of the

deuterated compounds was then performed analogously[5]). Reduction of the ketones **16** [8] and **26** [9] with $LiAlH_4$ or $LiAlD_4$ followed by hydrogenation gave the 3$\beta$-alcohols **17** [8a,b][10] and **27** [9b][11] and the (3$\alpha$-D)-isomers **17′** and **27′**[6]). The 3$\beta$-mesylates **18**, **18′**, **28**, and **28′** were then transformed under forced conditions [2] to the olefins **19** [12], **19′**, **29** [11], and **29′**. Treatment with dimethyldioxirane [7] afforded the $\beta$-epoxides **20**, **20′**, **30**, and **30′**. Epoxide opening with $PPh_3/I_2$ according to [13] followed by acetylation furnished the 2$\beta$-iodo 3$\alpha$-acetates **21**, **21′**, **31**, and **31′**[7]). The I-substituent was exchanged under $S_N2$-conditions after reaction with peracetic acid [14][8]) to afford the 2$\alpha$,3$\alpha$-diol 3$\alpha$-acetates **22**, **22′**, **32**, and **32′**[9]). The 2$\alpha$,3$\alpha$-diols **24**, **24′**, **34** and **34′** and the final target compounds, the 2$\alpha$,3$\alpha$-diol 2$\alpha$-tosylates **25**, **25′**, **35**, and **35′** were prepared by standard procedures (*Scheme 5*).

3.3. *Reactions of the (±)*-trans-*Decalins* **25** *and* **25′** *and of the (±)-Podocarpanes* **35** *and* **35′**. The unexpected reactions that were detected in the tetracyclic diterpenoid series could be reproduced with the model compounds (*Scheme 6*). Hence, upon reaction with $LiAlH_4$ the 2$\alpha$,3$\alpha$-diol 2$\alpha$-tosylates **25** and **35** afforded the 3$\beta$-alcohols **17** and **27**, and thermal reaction (pyridine or toluene) or base treatment (NaOEt or NaH) gave the ketones **36** [8a][10] and **37** [9].

Finally, treatment of the (3$\beta$-D)-2$\alpha$,3$\alpha$-diol 2$\alpha$-tosylates **25′** and **35′** with $LiAlH_4$ afforded the 3$\beta$-hydroxy (2$\beta$-D)-isomers **38** and **39**. The location of the D-atom was unambiguously inferred from the comparison of the $^1$H- and $^{13}$C-NMR data of the ring-A H- and C-atoms with those of the unlabeled isomers (see *Exper. Part*). However, the attempts to obtain the (2$\beta$-D)-3-ketones **36′** and **37′** by thermal reactions of **25′** and **35′** as described above were not successful. Only when the decalin **25′** was treated with NaOEt or NaH at room temperature, the expected **36′** could be evidenced (see *Exper. Part*); in all other experiments, just the unlabeled ketones **36** or **37** were isolated. This partial failure can be explained by the stereoelectronically favored enolization of the axial D–C(2), as demonstrated by the slow D-exchange when the neat compounds **36′** and **37′**[10]) were kept in solution at room temperature.

**3. Conclusions and Remarks.** – In spite of the restrictions mentioned above, the experimental results clearly disclose the mechanistic course of the investigated reaction. *The key step is a stereospecific C(3)* $\rightarrow$ *C(2)-hydride shift followed by an elimination process,* fully in accord with the postulated pathway depicted in *Scheme 3*. Moreover, as this course was shown to proceed with three different skeletal types

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5) As the steps for the preparation of the podocarpanes are identical to those of the decalins, the description of the individual synthetic pathways are combined (see also *Scheme 5*).

6) The structurally relevant spectroscopic data are similar for the podocarpanes and the phyllocladanes (see *Exper. Part*).

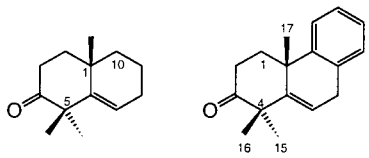
7) Ring A adopts the boat conformation, the big I-substituent being in the favorable equatorial position in **21** and **21′** and **31** and **31′** (see $^1$H-NMR signals of H–C(2) in the *Exper. Part*).

8) Usually, this transformation is now performed with MCPBA [5][15]. We had useful yields only when applying the original conditions [14].

9) Acyl migration ($\rightarrow$ **23**, **23′**, **33**, and **33′**) was observed when transforming **21**, **21′**, **31**, and **31′**, see *Exper. Part.*

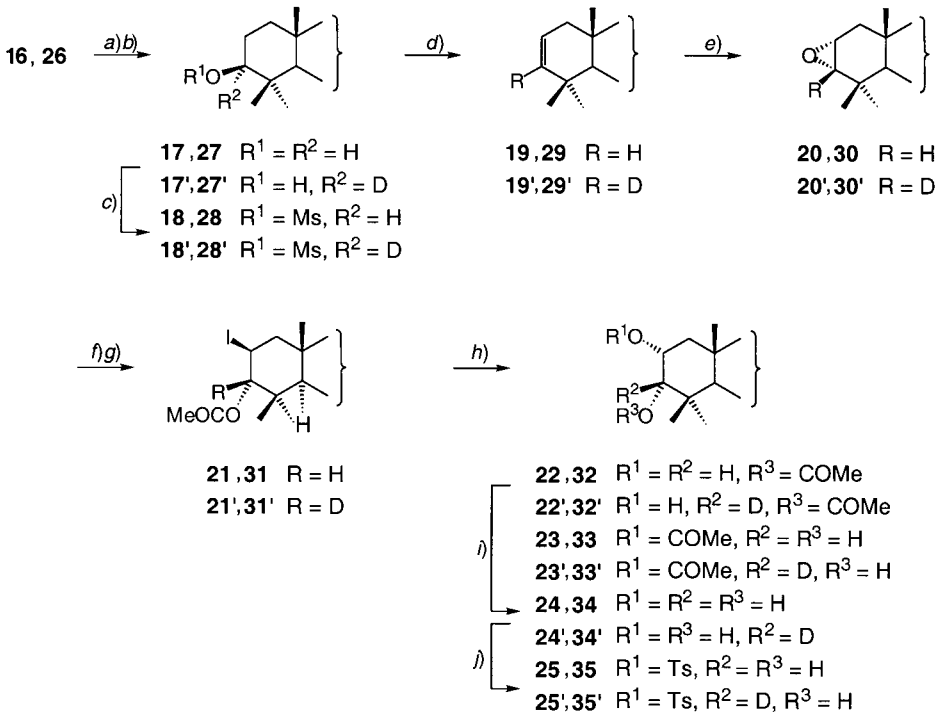
10) The key reference compounds **36′** and **37′** were accessible after *Jones* oxidation of **38** and **39**, respectively (*Scheme 6* and *Exper. Part*).

*Scheme 5*



**16** **26**

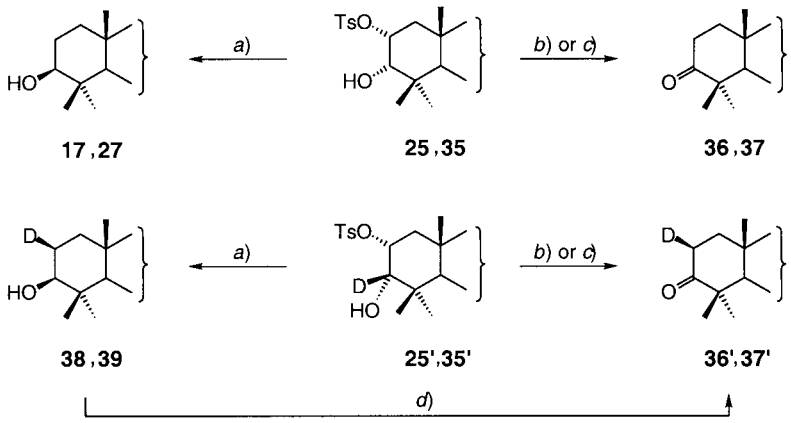
**17 - 25** = decalin-type ((±)-*trans*-1,5,5-trimethylbicyclo[4.4.0]decanes)
**27 - 35** = podocarpane-type (±)-*trans*-1,2,3,4,4a,9,10,10a-octahydro-1,1,4a-trimethyl-phenanthrenes)




*a*s) $LiAlH_4$ or $LiAlD_4$, THF, 0°. *b*) $H_2$, Pd/C, EtOH; **17** (75%), **17′** (92%), **27** (88%), **27′** (88%). *c*) $MeSO_2Cl$, pyridine, r.t.; **18** (66%), **18′** (67%), **28** (54%), **28′** (54%). *d*) LiBr, $Li_2CO_3$, DMF, 140°; **19** (67%), **19′** (95%), **29** (79%), **29′** (89%). *e*) Dimethyldioxirane (0.1M), $CH_2Cl_2$, −30° → r.t.; **20** (76%), **20′** (61%), **30** (66%), **30′** (60%). *f*) $PPh_3$, $I_2$, $Ch_2Cl_2$, r.t. *g*) $Ac_2O$, pyridine, r.t.; **21** (69%), **21′** (75%), **32** (85%), **31′** (82%). *h*) MeCOOOH (40%), $CH_2Cl_2$, r.t.; **22** (45%), **22′** (49%), **23** (13%), **23′** (11%), **32** (43%), **32′** (47%). *i*) $LiAlH_4$, THF, 0°; **24** (85%), **24′** (91%), **34** (76%), **34′** (74%). *j*) TsCl, pyridine, r.t.; **25** (93%), **25′** (96%), **35** (73%), **35′** (73%).

(phyllocladanes, decalins, and podocarpanes), the reaction mechanism seems to be a general feature of such 3$\alpha$,4$\alpha$-dioxy-substituted 1,5,5-trimethylbicyclo[4.4.0]decane congeners. It is noteworthy that the prerequisite for such a hydride shift is a good

*Scheme 6*




*a*) $LiAlH_4$, THF, r.t.; **17** (86%), **27** (85%), **38** (83%), **39** (89%). *b*) Pyridine, Δ: **36** (87%), **37** (86%); or toluene, Δ: **36** (90%), **37** (91%). *c*) NaOEt, r.t.: **36** (51%), **36/36′** (47%, *ca.* 6:1), **37** (57%); or NaH, r.t.: **36** (47%), **36/36′** (47%, *ca.* 6:1), **37** (57%). *d*) *Jones* reagent, r.t.; **36** (83%), **36′** (87%), **37** (87%), **37′** (86%). **17**, **25**, **25′**, **36**, **36′**, **38** = (±)-decalins **27**, **35**, **35′**, **37**, **37′**, **39** = (±)-podocarpanes

electrophilic leaving group at C(3), either in the starting material or at least in an intermediate as depicted in *Scheme 2* (pathway *b*)).

Related reactions of 2- or 3-(tosyloxy)lanosterol derivatives and selected D-labeled isomers thereof have been investigated by the group of *Levisalles* [16]. Besides the expected olefins, the reaction mixtures that were obtained after treatment with AcOH/NaOAc contained also significant amounts of products with a surprising distribution of D-atoms. These findings were rationalized by rather complex and – to some extent – speculative mechanisms [16]. In particular, the formation of each unexpected compound was explained by an individual and specific pathway that holds only for the respective reaction and its products. Based on our results, all of these reactions can now be simplified and generalized in terms of hydride shifts similar to those shown in the key steps of *Scheme 3*.

The authors are indebted to the *Swiss National Science Foundation* for financial support and to the analytical department of our institute for the MS and the *AMX-600* and *DRX-600* NMR spectra.

## Experimental Part

1. *General*. See [1].

2. *(16*R*)-16,17-(Isopropylidenedioxy)phyllocladan-3-one* (= *Calliterpenone 16,17-Acetonide*; **5b**). A soln. of **6** (610 mg) in abs. $CH_2Cl_2$ (15 ml) was added in one portion to a well-stirred suspension of pyridinium chlorochromate (PCC; 815 mg) and a trace of NaOAc in abs. $CH_2Cl_2$ (20 ml). The mixture was stirred at r.t. (2.5 h). Then, abs. $Et_2O$ was added and the supernatant liquid decanted from a black tar. The insoluble residue was washed with abs. $Et_2O$ (3×), the combined org. soln. passed through silica gel ($Et_2O$), and the solvent evaporated: **5b** (576 mg, 95%). White solid. $^1$H-NMR (300 MHz, $CDCl_3$): 4.08, 3.91 (*AB*, $^2J$ = 8.6, $CH_2$(17)); 2.51 (*ddd*, $^2J$ = 15.8, $^3J$(2ax,1ax) = 10.6, $^3J$(2ax,1eq) = 7.3, $H_{ax}$–C(2)); 2.37 (*ddd*, $^2J$ = 15.8, $^3J$(2eq,1ax) = 7.2, $^3J$(2eq,1eq) = 4.2, $H_{eq}$–C(2)); 2.24 (*dd*, $^2J$ = 15.8, $^4J$(15$\beta$,14ax) = 2.2, $H_\beta$–C(15)); 2.01 (*m*, *q*-like, $w_{1/2} \approx 9$, H–C(13)); 1.95–1.83 (*m*, $H_{eq}$–C(1), $H_{eq}$–C(14)); 1.39, 1.35 (2*s*, $Me_2C(O)_2$)); 1.07 (*s*, Me(18)); 1.02 (*s*, Me(20)); 0.98 (*s*, Me(19)).

3. *Ketone* **5b** *from Diol* **2** *and from Tosylate* **3**. *a*) TsCl (22 mg) was added to a soln. of **2** [1] (11.5 mg) in abs. pyridine (2 ml). The mixture was refluxed (18 h). Then $H_2O$ was added and the mixture extracted with $Et_2O$. The org. phase was washed with $H_2O$, dried ($MgSO_4$), and evaporated, and the residue purified by CC (hexane/AcOEt 1:1): **5b** (5.4 mg, 50%) as a white foam and unchanged **2** (5.2 mg, 47%).

*b*) A soln. of **3** [1] (5 mg) in abs. pyridine (4 ml) was refluxed (18 h). Workup and CC as described in *a*) gave **5b** (3 mg, 89%).

*c*) A soln. of **3** (5 mg) in abs. toluene (4 ml) was refluxed (18 h). Workup and CC as described in *a*) gave **5b** (3.3 mg, 98%).

*d*) NaOEt (6 mg) was added to a soln. of **3** (6 mg) in abs. THF (2 ml), and the mixture was stirred at r.t. (2 h). Workup and prep. TLC (hexane/AcOEt 1:1) gave **5b** (2.1 mg, 52%).

*e*) NaH (80% suspension in oil; 7 mg) was added to a soln. of **3** (6 mg) in abs. THF (2 ml), and the mixture was stirred at r.t. (2 h). Workup and purification as described in *d*) gave **5b** (2 mg, 49%).

4. *(3*S*,16*R*)-16,17-(Isopropylidenedioxy)phyllocladan-3-ol 3-(Methanesulfonate)* (**7**) *and (3*S*,16*R*)-16,17-(Isopropylidenedioxy(3-*$^2$*H)phyllocladane-3-ol 3-(Methanesulfonate)* (**7′**). Methanesulfonyl chloride (70 µl) was added to a soln. of **6** [1] (64 mg) in abs. pyridine (2 ml), and the mixture was kept at r.t. (40 h). Then $H_2O$ was added and the mixture extracted with $Et_2O$. Workup and CC (hexane/AcOEt 5:1) yielded **7** (73 mg, 94%). White solid. $^1$H-NMR (300 MHz, $CDCl_3$): 4.34 (*m*, *dd*-like, H–C(3)); 4.05, 3.89 (*AB*, $^2J = 8.6$, $CH_2$(17)); 3.00 (*s*, $MeSO_3$); 2.23 (*dd*, $^2J = 14.6$, $^4J(15\beta,14ax) = 2.1$, $H_\beta$–C(15)); 1.98 (*m*, $w_{1/2} \approx 8$, H–C(13)); 1.38, 1.34 (2*s*, $Me_2C(O)_2$); 1.01 (*s*, Me(18)); 0.90 (*s*, Me(20)); 0.85 (*s*, Me(19)).

Analogous treatment of **6′** [1] (56 mg) afforded **7′** (57 mg, 84%). White solid. $^1$H-NMR (300 MHz, $CDCl_3$): 4.06, 3.89 (*AB*, $^2J = 8.6$, $CH_2$(17)); 3.01 (*s*, $MeSO_3$); 2.23 (*dd*, $^2J = 14.6$, $^4J(15\beta,14ax) = 2.1$, $H_\beta$–C(15)); 1.98 (*m*, $w_{1/2} \approx 8$, H–C(13)); 1.38, 1.34 (2*s*, $Me_2C(O)_2$); 1.01 (*s*, Me(18)); 0.90 (*s*, Me(20)); 0.85 (*s*, Me(19)).

5. *(16*R*)-16,17-(Isopropylidenedioxy)phylloclad-2-ene* (**8**) *and (16*R*)-16,17-(Isopropylidenedioxy)(3-*$^2$*H)phylloclad-2-ene* (**8′**). The mixture of **7** (70 mg), LiBr (42 mg), and $Li_2CO_3$ (40 mg) in abs. dimethylformamide (2 ml) was refluxed (1 h). Workup and CC (hexane/AcOEt 10:1) yielded **8** (47 mg, 86%). Clear, colorless needles. IR ($CHCl_3$): 2988, 2937, 2864, 1456, 1381, 1371, 1244, 1176, 1157, 1107, 1052, 1022, 986, 891. $^1$H-NMR (300 MHz, $CDCl_3$): 5.38 (*m*, 2 H, H–C(2), H–C(3)); 4.08, 3.92 (*AB*, $^2J = 8.6$, $CH_2$(17)); 2.30 (*dd*, $^2J = 14.5$, $^4J(15\beta,14ax) = 2.1$, $H_\beta$–C(15)); 1.99 (*m*, $w_{1/2} \approx 9$, H–C(13)); 1.89 (*ddd*, $^2J = 11.1$, $^3J(14eq,13) = 4.8$, $^4J(14eq,12eq) = 2.5$, $H_{eq}$–C(14)); 1.39, 1.35 (2*s*, $Me_2C(O)_2$); 0.94 (*s*, Me(20)); 0.89 (*s*, Me(19)); 0.86 (*s*, Me(18)). CI-MS: 362 (5, $[M + NH_4]^+$), 345 (15, $[M + H]^+$), 329 (49, $[M - CH_3]^+$), 304 (100, $[M - C_3H_4]^+$).

Analogous treatment of **7′** (56 mg) afforded **8′** (40 mg, 92%). White crystals. $^1$H-NMR (300 MHz, $CDCl_3$): 5.38 (*dd*, $^3J(2,1ax) = 6.0$, $^3J(2,1eq) = 1.7$, 1 H, H–C(2)); 4.08, 3.92 (*AB*, $^2J = 8.6$, $CH_2$(17)); 2.30 (*dd*, $^2J = 14.5$, $^4J(15\beta,14ax) = 2.1$, $H_\beta$–C(15)); 1.99 (*m*, $w_{1/2} \approx 9$, H–C(13)); 1.89 (*ddd*, $^2J = 11.1$, $^3J(14eq,13) = 4.8$, $^4J(14eq,12eq) = 2.5$, $H_{eq}$–C(14)); 1.39, 1.35 (2*s*, $Me_2C(O)_2$); 0.94 (*s*, Me(20)); 0.89 (*s*, Me(19)); 0.86 (*s*, Me(18)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 137.6 (*t*, $^1J$ (C,D) = 23.5, C(3)); 121.2 (C(2)); 108.4 ($Me_2C(O)_2$); 91.6 (C(16)); 69.9 (C(17)); 55.1 (C(9)); 52.1 (C(5)); 49.1 (C(14)); 47.7 (C(15)); 44.4 (C(13)); 43.9 (C(8)); 40.4 (C(7)); 40.0 (C(1)); 36.5 (C(10)); 33.7 (C(18)); 34.4 (C(4)); 31.9 C(19)); 27.9 (C(12)); 27.0, 26.8 ($Me_2C(O)_2$); 22.9 (C(18)); 21.2 (C(6)); 20.0 (C(11)); 18.4 (C(2)); 15.3 (C(20)).

6. *Hydroxy Esters* **11**, **11′**, **12**, *and* **12′**. $NaBH_4$ (3 mg) was added to a soln. of **9** [1] (9.5 mg) in abs. THF (2 ml) and stirred at r.t. (3 d). Then $H_2O$ was added and the soln. extracted with $Et_2O$. The org. phase was washed with $H_2O$, dried ($MgSO_4$), and evaporated and the residue purified by prep. TLC (toluene/AcOEt 5:2): *(2*R*,3*R*,16*R*)-16,17-(isopropylidenedioxy)phyllocladane-2,3-diol 2-(3-methylbut-2-enoate)* (**11**; 4.9 mg, 51%) and *(2*R*,3*R*,16*R*)-16,17-(isopropylidenedioxy)phyllocladane-2,3-diol 3-(3-methylbut-2-enoate)* (**12**; 2.3 mg, 24%) both as white crystals.

*Data of* **11** (300 MHz, $CDCl_3$): 5.68 (*m*, *t*-like, H–C(2′)); 4.96 (*ddd*, $^3J(2,1ax) = 11.8$, $^3J(2,3) = 10.1$, $^3J(2,1eq) = 4.5$, H–C(2)); 4.05, 3.89 (*AB*, $^2J = 8.6$, $CH_2$(17)); 3.20 (*d*, $^3J(3,2) = 10.1$, H–C(3)); 2.24 (*dd*, $^2J = 14.3$, $^4J(15\beta,14ax) = 1.8$, $H_\beta$–C(15)); 2.17, 1.90 (2*d*, $^4J(4',2') = {}^4J(Me–C(3'),2') = 1.2$, Me(4′), Me–C(3′)); 1.38, 1.34 (2*s*, $Me_2C(O)_2$); 1.04 (*s*, Me(18)); 1.00 (*s*, Me(20)); 0.86 (*s*, Me(19)).

*Data of* **12**: (300 MHz, $CDCl_3$): 5.76 (*m*, *t*-like, H–C(2′)); 4.51 (*d*, $^3J(3,2) = 0.1$, H–C(3)); 4.07, 3.89 (*AB*, $^2J = 8.6$, $CH_2$(17)); 3.80 (*ddd*, $^3J(2,1ax) = 11.8$, $^3J(3,2) = 10.1$, $^3J(2,1eq) = 4.5$, H–C(2)); 2.19, 1.92 (2*d*, $^4J(4',2') = {}^4J(Me–C(3'),2') = 1.1$, Me(4′), Me–C(3′)); 1.38, 1.34 (2*s*, $Me_2C(O)_2$); 0.95 (*s*, Me(18)); 0.89 (*s*, Me(20)); 0.87 (*s*, Me(19)).

Analogous treatment of **9** [1] (75 mg) with $NaBD_4$ (100 mg) in abs. THF (5 ml) gave after CC (hexane/AcOEt 1:1) *(2*R*,3*R*,16*R*)-16,17-(isopropylidenedioxy)(3-*$^2$*H)phyllocladane-2,3-diol 2-(3-methylbut-2-enoate)* (**11′**; 39 mg, 52%) and *(2*R*,3*R*,16*R*)-16,17-(isopropylidenedioxy)(3-*$^2$*H)phyllocladane-2,3-diol 3-(3-methylbut-2-enoate)* (**12′**, 18 mg, 24%), both as white crystals.

*Data of* **11′**: $^1$H-NMR (300 MHz, $CDCl_3$): 5.68 (*m*, *t*-like, H–C(2′)); 4.95 (*dd*, $^3J$(2,1ax) = 11.4, $^3J$(2,1eq) = 4.6, H–C(2)); 4.05, 3.90 (*AB*, $^2J$ = 8.6, $CH_2$(17)); 2.24 (*dd*, $^2J$ = 14.3, $^4J$(15$\beta$,14ax) = 1.8, $H_\beta$–C(15)); 2.17, 1.90 (2*d*, $^4J$(4′,5′) = $^4J$(Me–C(3′),2′) = 1.2, Me(4′), Me–C(3′)); 1.38, 1.34 (2*s*, $Me_2C(O)_2$); 1.04 (*s*, Me(18)); 1.00 (*s*, Me(20)); 0.86 (*s*, Me(19)).

*Data of* **12′**: $^1$H-NMR (300 MHz, $CDCl_3$): 5.76 (*m*, *t*-like, H–C(2′)); 4.07, 3.89 (*AB*, $^2J$ = 8.6, $CH_2$(17)); 3.80 (*dd*, $^3J$(2,1ax) = 11.8, $^3J$(2,1eq) = 4.5, H–C(2)); 2.19, 1.92 (each *d*, $^4J$(4′,5′) = $^4J$(Me–C(3′),2′) = 1.1, Me(4′), Me–C(3′)); 1.38, 1.34 (2*s*, $Me_2C(O)_2$); 0.95 (*s*, Me(18)); 0.88 (*s*, Me(20)); 0.87 (*s*, Me(19)).

7. *(2*R,*3*R,*16*R*)-16,17-(Isopropylidenedioxy)phyllocladane-2,3-diol 2-(4-Methylbenzenesulfonate)* (**13**). $LiAlH_4$ (50 mg) was added to a soln. of **9** [1] (35 mg) in abs. THF (4 ml) and stirred at r.t. (30 min). Then EtOH and $H_2O$ were added followed by some dil. $H_2SO_4$ soln. to dissolve the precipitate. The soln. was extracted with $Et_2O$, the org. phase washed with $H_2O$, dried ($MgSO_4$), and evaporated. The crude residue (30 mg) was dissolved in abs. pyridine (2 ml). TsCl (40 mg) was added and the mixture kept at r.t. (3 d). Workup and CC (hexane/AcOEt 1:1) gave **13** (6.5 mg, 16%). White foam. $^1$H-NMR (300 MHz, $CDCl_3$): 7.81, 7.35 (*AA′BB′*, *J* = 8.3, arom. H); 4.63 (*ddd*, $^3J$(2,1ax) = 11.6, $^3J$(2,3) = 9.8, $^3J$(2,1eq) = 4.7, H–C(2)); 4.04, 3.89 (*AB*, $^2J$ = 8.6, $CH_2$(17)); 3.17 (*d*, $^3J$(3,2) = 9.8, H–C(3)); 2.45 (*s*, *Me*$C_6H_4$); 2.18 (*dd*, $^2J$ = 14.5, $^4J$(15$\beta$,14ax) = 2.2, $H_\beta$–C(15)); 1.89 (*ddd*, $^2J$ = 1.2, $^3J$(14eq,13) = 4.8, $^4J$(14eq,12eq) = 2.4, $H_{eq}$–C(14)); 1.38, 1.34 (2*s*, $Me_2C(O)_2$); 1.02 (*s*, Me(18)); 0.90 (*s*, Me(20)); 0.79 (*s*, Me(19)).

8. *(2*R,*3*S,*16*R*)-2,3-Epoxy-16,17-(isopropylidenedioxy)phyllocladane* (**14**) *and (2*R,*3*S,*16*R*)-2,3-Epoxy-16,17-(isopropylidenedioxy)(3-$^2$H)phyllocladane* (**14′**). At −30°, 0.1M dimethyldioxirane in acetone [7] (2 ml) was added to **8** (35 mg) in abs. $CH_2Cl_2$ (4 ml), and the mixture was stirred at r.t. (15 h). Evaporation and CC (hexane/AcOEt 10:1) gave **14** (14 mg, 38%). White needles. IR ($CHCl_3$): 3016, 2988, 2937, 2865, 1456, 1381, 1371, 1244, 1206, 1151, 1052, 891, 826. $^1$H-NMR (600 MHz, $CDCl_3$): 4.06, 3.90 (*AB*, $^2J$ = 8.6, $CH_2$(17)); 3.16 (*dd*, $^3J$(2,1eq) = 6.2, $^3J$(2,3) = 3.9, H–C(2)); 2.78 (*d*, $^3J$(3,2) = 3.9, H–C(3)); 2.10 (*dd*, $^2J$ = 14.5, $^4J$(15$\beta$,14ax) = 2.1, $H_\beta$–C(15)); 1.98 (*m*, $w_{1/2} \approx 11$, H–C(13)); 1.92 (*dd*, $^2J$(1eq,1ax) = 14.9, $^3J$(1eq,2) = 6.2, $H_{eq}$–C(1)); 1.85 (*ddd*, $^2J$(14eq,14ax) = 11.3, $^3J$(14eq,13) = 4.8, $^4J$(14eq,12eq) = 2.4, $H_{eq}$–C(14)); 1.68 (*m*, $w_{1/2} \approx 27$, $H_{eq}$–C(12)); 1.38, 1.34 (2*s*, $Me_2C(O)_2$); 1.08 (*s*, Me(18)); 0.98 (*s*, Me(20)); 0.86 (*s*, Me(19)). $^{13}$C-NMR (150.9 MHz, $CDCl_3$): 108.4 (*Me*$_2$C(O)$_2$); 91.4 (C(16)); 69.8 (C(17)); 61.5 (C(3)); 54.7 (C(9)); 52.3 (C(2)); 48.7 (C(14)); 47.4 (C(15)); 47.1 (C(5)); 44.3 (C(13)); 43.6 (C(8)); 40.2 (C(7)); 39.4 (C(1)); 36.2 (C(10)); 32.5 (C(4)); 28.2 (C(18)); 27.8 (C(12)); 27.0, 26.8 (*Me*$_2$C(O)$_2$); 22.3 (C(19)); 20.4 (C(6)); 19.9 (C(11)); 17.5 (C(20)). CI-MS: 378 (23, $[M + NH_4]^+$), 361 (14, $[M + H]^+$), 345 (86, $[M - Me]^+$), 343 (30, $[M - OH]^+$), 320 (45), 285 (100).

Analogous treatment of **13′** (30 mg) afforded **14′** (12 mg, 38%). White needles. $^1$H-NMR (300 MHz, $CDCl_3$): 4.06, 3.90 (*AB*, $^2J$ = 8.6, $CH_2$(17)); 3.16 (*d*, $^3J$(2,1eq) = 6.2, $^3J$(2,1ax) ≈ 0, H–C(2)); 2.10 (*dd*, $^2J$ = 14.5, $^4J$(15$\beta$,14ax) = 2.1, $H_\beta$–C(15)); 1.98 (*m*, $w_{1/2} \approx 11$, H–C(13)); 1.92 (*dd*, $^2J$ = 4.9, $^3J$(1eq,2) = 6.2, $H_{eq}$–C1)); 1.85 (*ddd*, $^2J$ = 11.3, $^3J$(14eq,13) = 4.8, $^4J$(14eq,12eq) = 2.4, $H_{eq}$–C(14)); 1.68 (*m*, $w_{1/2} \approx 27$, $H_{eq}$–C(12)); 1.38, 1.34 (2*s*, $Me_2C(O)_2$); 1.08 (*s*, Me(18)); 0.98 (*s*, Me(20)); 0.86 (*s*, Me(19)).

9. *(2*S,*3*R,*16*R*)-2,3-Epoxy-16,17-(isopropylidenedioxy)phyllocladane* (**15**). Treatment of **13** (5 mg) in abs. THF (3 ml) with $LiAlH_4$ (30 mg) at r.t. (40 h) gave, after prep. TLC ((hexane/acetone 9:1), **15** (2 mg, 68%). Colorless oil that crystallized after several weeks to yield suitable crystals for an X-ray analysis. IR ($CHCl_3$): 2971, 2931, 2856, 1727, 1460, 1370, 1245, 1150, 1050. $^1$H-NMR (600 MHz, $CDCl_3$): 4.07, 3.91 (*AB*, $^2J$ = 8.6, $CH_2$(17)); 3.23 (*ddd*, $^3J$(2,1ax) = 4.3, $^3J$(2,3) = 4.0, $^3J$(2,1eq) = 2.2, H–C(2)); 2.83 (*d*, $^3J$(3,2) = 4.0, H–C(3)); 2.22 (*dd*, $^2J$ = 14.5, $^4J$(15$\beta$,14ax) = 2.2, $H_\beta$–C(15)); 2.14 (*dd*, $^2J$ = 1 5.0, $^3J$(1eq,2) = 2.2, $H_{eq}$–C(1)); 1.98 (*m*, *q*-like, $w_{1/2} \approx 9$, H–C(13)); 1.86 (*ddd*, $^2J$ = 11.2, $^3J$(14eq,13) = 4.7, $^4J$(14eq,12eq) = 2.4, $H_{eq}$–C(14)); 1.37, 1.34 (2*s*, $Me_2C(O)_2$); 1.06 (*s*, Me(18)); 1.02 (*s*, Me(20)); 0.98 (*s*, Me(19)). $^{13}$C-NMR (150.9 MHz, $CDCl_3$): 108.3 ($Me_2$*C*(O)$_2$); 69.8 (C(17)); 61.0 (C(3)); 56.5 (C(9)); 54.3 (C(2)); 52.2 (C(5)); 49.3 (C(15)); 47.8 (C(14)); 44.2 (C(13)); 40.5 (C(7)); 37.8 (C(1)); 30.3 (C(18)); 27.8 (C(12)); 26.8 (2 C, *Me*$_2$C(O)$_2$); 21.3 (C(6)); 20.6 (C(19)); 20.4 (C(11)); 16.5 (C(20)). CI-MS: 378 (< 5, $[M + NH_4]^+$), 345 (16, $[M - Me]^+$), 320 (87, $[M - C_3H_4]^+$), 302 (6, $[M - C_3H_4 - H_2O]^+$), 285 (23, $[M - C_3H_4 - H_2O - CH_3]^+$), 131 (100). EI-MS: 360 (< 5, $M^{+\bullet}$), 345 (100, $[M - Me]^+$).

10. *(1*RS,*6*SR*)-1,5,5-Trimethylbicyclo[4.4.0]decanes* ((±)-trans-*Decalins* = *(±)*-trans-*Decahydronaphthalenes*) **17**–**25** *and* **17′**–**25′**. *(1*RS,*4*RS,*6*SR*)-1,5,5-Trimethylbicyclo[4.4.0]decan-4-ol* (= *(2*RS,*4a*RS,*8a*SR*)-Decahydro-1,1,4a-trimethylnaphthalen-2-ol;* **17**) *and (1*RS,*4*RS,*6*SR*)-1,5,5-Trimethyl(4-$^2$H)bicyclo[4.4.0]decan-4-ol* (**17′**). To a soln. of **16** [8] (4.1 g) in abs. THF (20 ml), $LiAlH_4$ (2 g) was added in portions at 0°, and the mixture was stirred at r.t. (1 h). After workup as described in *Exper. 7* the residue was dissolved in abs. EtOH (25 ml) and stirred in the presence of 10% Pd/C (1 g) under a slight $H_2$ pressure at r.t. (15 h). Bulb-to-bulb distillation at 150°/0.05 Torr gave **17** [8a,b] [10] (3.14 g, 75%). Viscous, yellowish oil. $^1$H-NMR (600 MHz, $CDCl_3$): 3.22 (*m*, *dd*-like, $^3J$(4,3ax) ≈ 9, $^3J$(4,3eq) ≈ 7, H–C(4)); 1.80 (*m*, $H_{eq}$–C(8), OH); 1.62 (*m*, *dt*-like, $CH_2$(3); 1.60 (*m*, *dq*-

like, $^2J$ = 13.5, $H_{eq}$–C(7)); 1.42 (br. *m*, $CH_2$(9)); 1.40 (*m*, *dt*-like, $H_{eq}$–C(2)), 1.31 (*m*, *dt*-like, $H_{eq}$–C(10)); 1.25 (*m*, *dt*-like, $^2J$ = 13.5, $H_{ax}$–C(7)); 1.2 (br. *m*, $H_{ax}$–C(2), $H_{ax}$–C(8)); 1.03 (br. *m*, $H_{ax}$–C(10)); 0.96 (*s*, $Me_{eq}$–C(5)); 0.91 (*s*, Me–C(1)); 0.83 (*dd*, $^3J$(6,7ax) = 12.0, $^3J$(6,7eq) = 2.7, H–C(6)); 0.75 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (150 MHz, $CDCl_3$): 79.3 (C(4)); 52.7 (C(6)); 45.2 (C(10)); 40.2 (C(2)); 38.8 (C(5)); 34.1 (C(1)); 27.8 ($Me_{eq}$–C(5)); 27.6 (C(3)); 27.5 (C(8)); 21.7 (C(9)); 21.6 (C(7)); 19.2 (*Me*–C(1)); 15.0 ($Me_{ax}$–C(5)). EI-MS: 196 (18, $M^{+\bullet}$), 181 (8, $[M-CH_3]^+$), 163 (53, $[M-CH_3-H_2O]^+$), 83 (100).

Analogous treatment of **16** (2.02 g) with $LiAlD_4$ (1.3 g) afforded **17′** (2.06 g, 92%) after bulb-to-bulb distillation at 120°/0.01 Torr. Clear oil. IR ($CHCl_3$): 3614, 2931, 2850, 1458, 1382, 1366, 1286, 1170, 1132, 1084, 1061, 1040, 1016, 931. $^1$H-NMR (300 MHz, $CDCl_3$): 1.80 (*m*, $H_{eq}$–C(8), OH); 1.62 (*m*, $CH_2$(3); 1.60 (*m*, *dq*-like, $H_{eq}$–C(7)); 1.42 (*m*, $CH_2$(9)); 1.40 (*m*, *dt*-like, $H_{eq}$–C(2)), 1.31 (*m*, *dt*-like, $H_{eq}$–C(10)); 1.25 (*m*, $H_{ax}$–C(7)); 1.2 (*m*, $H_{ax}$–C(2), $H_{ax}$–C(8)); 1.03 (*m*, $H_{ax}$–C(10)); 0.95 (*s*, $Me_{eq}$–C(5)); 0.91 (*s*, Me–C(1)); 0.83 (*dd*, $^3J$(6,7ax) = 12.0, $^3J$(6,7eq) = 2.7, H–C(6)); 0.75 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 78.8 (*t*, $^1J$ (C,D) = 21.4, C(4)); 52.7 (C(6)); 45.2 (C(10)); 40.2 (C(2)); 38.7 (C(5)); 34.1 (C(1)); 27.7 ($Me_{eq}$–C(5)); 27.5 (C(3)); 27.4 (C(8)); 21.8 (C(9)); 21.7 (C(7)); 19.2 (*Me*-C(1)); 15.0 ($Me_{ax}$–C(5)). EI-MS: 197 (15, $M^{+\bullet}$), 182 (8, $[M-CH_3]^+$), 164 (42, $[M-CH_3-H_2O]^+$), 83 (100).

*(1*RS*,4*RS*,6*SR*)-1,5,5-Trimethylbicyclo[4.4.0]decan-4-ol Methanesulfonate* (= *(2*RS*,4a*RS*,8a*SR*)-Decahydro-1,1,4a-trimethylnaphthalen-2-ol Methanesulfonate;* **18**) *and (1*RS*,4*RS*,6*SR*)-1,5,5-Trimethyl(4-$^2$H)bicyclo[4.4.0]decan-4-ol Methanesulfonate* (**18′**). Reaction of **17** (3.0 g) in abs. pyridine (25 ml) with methanesulfonyl chloride (3.5 ml) as described in *Exper. 4* gave **18** (2.75 g, 66%), after CC (hexane/AcOEt 30:1). Clear yellowish oil that crystallized after a few days. M.p. 32–35°. $^1$H-NMR (300 MHz, $CDCl_3$): 4.34 (*dd*, $^3J$(4,3ax) = 9.5, $^3J$(4,3eq) = 7.0, H–C(4)); 3.01 (*s*, $MeSO_3$); 1.96 (*m, td*-like, $CH_2$(3)); 1.8–1.0 (*m*, 11 H); 1.00 (*s*, $Me_{eq}$–C(5)); 0.95 (*s*, Me–C(1)); 0.93 (*dd*, $^3J$(6,7ax) = 12.0, $^3J$(6,7eq) = 2.7, H–C(6)); 0.84 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 90.7 (C(4)); 52.9 (C(6)); 44.8 (C(10)); 39.8 (C(2)); 38.8 ($MeSO_3$); 38.5 (C(5)); 33.9 (C(1)); 27.9 ($Me_{eq}$–C(5)); 27.2, 25.7, 21.6 (C(3), C(8), C(9)); 19.1 (*Me*–C(1)); 15.9 ($Me_{ax}$–C(5)).

Analogous treatment of **17′** (1.93 g) with methanesulfonyl chloride (1.9 ml) afforded **18′** (1.80 g, 67%). Clear oil. IR ($CHCl_3$): 3030, 2976, 2930, 2852, 1460, 1448, 1391, 1383, 1352, 1171, 1122, 1100, 1029, 1012, 970, 912, 850. $^1$H-NMR (300 MHz, $CDCl_3$): 3.01 (*s*, $MeSO_3$); 1.96 (*m*, *dd*-like, $CH_2$(3)); 1.8–1.0 (*m*, 11 H); 1.00 (*s*, $Me_{eq}$–C(5)); 0.95 (*s*, Me–C(1)); 0.93 (*dd*, $^3J$(6,7ax) = 12.0, $^3J$(6,7eq) = 2.7, H–C(6)); 0.84 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 90.3 (*t*, $^1J$(C,D) = 22.5, C(4)); 52.8 (C(6)); 44.8 (C(10)); 39.8 (C(2)); 38.8 ($MeSO_3$); 38.5 (C(5)); 33.9 (C(1)); 27.9 ($Me_{eq}$–C(5)); 27.2, 25.6, 21.6 (C(3), C(8), C(9)); 19.1 (*Me*–C(1)); 15.9 ($Me_{ax}$–C(5)). CI-MS: 293 (100, $[M+NH_4]^+$).

*(1*RS*,6*SR*)-1,5,5-Trimethylbicyclo[4.4.0]dec-3-ene* (= *(4a*RS*,8a*SR*)-1,2,3,4,4a,5,8,8a-Octahydro-5,5,8a-trimethylnaphthalene;* **19**) *and (1*RS*,6*SR*)-1,5,5-Trimethyl(4-$^2$H)bicyclo[4.4.0]dec-3-ene* (**19′**). The mixture of **18** (2.75 g), LiBr (2.61 g), and $Li_2CO_3$ (2.22 g) in abs. dimethylformamide (20 ml) was refluxed (2 h) and worked up as described in *Exper. 5*. The residue was bulb-to-bulb distilled at 100°/0.05 Torr: **19** [12] (1.20 g, 67%). Clear liquid. IR ($CHCl_3$): 3025, 3010, 2929, 2862, 1706, 1655, 1466, 1449, 1377, 1362, 1216, 1212, 1164, 1096, 1012, 987. $^1$H-NMR (300 MHz, $CDCl_3$): 5.47 (*ddd*, $^3J$(3,4) = 10.1, $^3J$(3,2eq) = 5.8, $^3J$(3,2ax) = 2.0, H–C(3)); 5.43 (*dd*, $^3J$(4,3) = 10.1, $^4J$(4,2ax) = 2.7, H–C(4)); 1.83 (*m*, *dq*-like, $H_{eq}$–C(7)); 1.79 (br. *d*, $^2J$ = 16.8, $H_{ax}$–C(2)); 1.70 (*dd*, $^2J$ = 16.8, $^3J$(2eq,3) = 5.8, $H_{eq}$–C(2)); 1.59 (*m*, *dd*-like, $H_{eq}$–C(9)); 1.50 (*m*, $CH_2$(8)); 1.43 (*m*, *dq*-like, $H_{eq}$–C(10)): 1.30 (*m*, *dd*-like, $H_{ax}$–C(9)); 1.28 (*m*, *dd*-like, H–C(6)); 1.27 (*m*, $H_{ax}$–C(7)); 1.14 (*m*, *dt*-like, $H_{ax}$–C(10)); 0.95 (*s*, Me–C(1)); 0.93 (*s*, $Me_{eq}$–C(5)); 0.84 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 138.3 (C(4)); 121.6 (C(3)); 50.0 (C(6)); 43.7 (C(10)); 41.8 (C(2)); 34.4 (C(5)); 33.0 (C(1)); 31.3 ($Me_{eq}$–C(5)); 27.7 (C(7)); 22.9 ($Me_{ax}$–C(5)); 22.8 (C(9)); 22.3 (C(8)); 19.2 (*Me*–C(1)). EI-MS: 178 (18, $M^{+\bullet}$), 163 (100, $[M-CH_3]^+$).

Reaction of **18′** (1.70 g) with LiBr (1.78 g) and $Li_2CO_3$ (1.44 g) in abs. dimethylformamide (15 ml) and CC (hexane) of the residue gave pure **19′** (1.05 g, 95%). Clear liquid. IR ($CHCl_3$): 2929, 2862, 1466, 1448, 1378, 1362, 1048. $^1$H-NMR (300 MHz, $CDCl_3$): 5.47 (*m*, $w_{1/2} \approx 12$, H–C(3)); 1.83 (*m*, *dq*-like, $H_{eq}$–C(7)); 1.79 (*dd*, $^2J$ = 16.8, $^3J$(2ax,3) = 2.0, $H_{ax}$–C(2)); 1.70 (*dd*, $^2J$ = 16.8, $^3J$(2eq,3) = 5.8, $H_{eq}$–C(2)); 1.59 (*m*, *dd*-like, $H_{eq}$–C(9)); 1.50 (*m*, $CH_2$(8)); 1.43 (*m*, *dq*-like, $H_{eq}$–C(10)): 1.30 (*m*, *dd*-like, $H_{ax}$–C(9)); 1.28 (*m*, *dd*-like, H–C(6)); 1.27 (*m*, $H_{ax}$–C(7)); 1.14 (*m*, *dt*-like, $H_{ax}$–C(10)); 0.95 (*s*, Me–C(1)); 0.93 (*s*, $Me_{eq}$–C(5)); 0.84 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 138.0 (*t*, $^1J$(C,D) = 23.6, C(4)); 121.4 (C(3)); 50.0 (C(6)); 43.7 (C(10)); 41.8 (C(2)); 34.2 (C(5)); 33.0 (C(1)); 31.3 ($Me_{eq}$–C(5)); 27.7 (C(7)); 22.9 ($Me_{ax}$–C(5)); 22.8 (C(9)); 22.3 (C(8)); 19.2 (*Me*–C(1)). EI-MS: 179 (21, $M^{+\bullet}$), 164 (100, $[M-CH_3]^+$), 123 (82).

*(1*RS*,3*SR*,4*RS*,6*SR*)-3,4-Epoxy-1,5,5-trimethylbicyclo[4.4.0]decane* (= *(1a*RS*,2a*SR*,6a*RS*,7a*SR*)-Decahydro-2a,7,7-trimethylnaphth[2,3-*b*]oxirene*; **20**) *and (1*RS*,3*SR*,4*RS*,6*SR*)-3,4-Epoxy-1,5,5-trimethyl(4-$^2$H)bicyclo[4.4.0]decane* (**20′**). At −30°, 0.1M dimethyldioxirane in acetone [7] (30 ml) was added to **19** (511 mg) in

abs. $CH_2Cl_2$ (10 ml) at $-30°$, and the mixture was stirred at r.t. (15 h). Evaporation and CC (hexane/AcOEt 30:1) gave **20** (425 mg, 76%). Clear oil with a resinous scent. IR ($CHCl_3$): 3025, 2932, 2862, 1465, 1448, 1388, 1381, 1366, 1237, 1224, 1218, 1210, 1066, 1002, 990, 936, 925, 894, 825, 816. $^1$H-NMR (300 MHz, $CDCl_3$): 3.19 (*ddd*, $^3J$(3,2eq) = 6.1, $^3J$(3,4) = 3.9, $^3J$(3,2ax) = 0.5, H–C(3)); 2.78 (*d*, $^3J$(2,3) = 3.9, H–C(2)); 1.73 (*dd*, $^2J$ = 15.1, $^3J$(2eq,3) = 6.1, $H_{eq}$–C(2)); 1.55–1.10 (*m*, 11 H); 1.07 (*s*, $Me_{eq}$–C(5)); 0.96 (*s*, Me–C(1)); 0.92 $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 62.0 (C(4)); 52.6 (C(3)); 45.1 (C(6)); 44.0 (C(10)); 41.3 (C(2)); 32.8 (C(1)); 32.4 (C(5)); 27.5 ($Me_{eq}$–C(5)); 27.3 (C(8)); 22.3 (C(9)); 22.1 (C(7)); 22.0, 21.5 (*Me*–C(1), $Me_{ax}$–C(5)). EI-MS: 194 (5, $M^{+\cdot}$), 179 (63, $[M-CH_3]^+$), 161 (83, $[M-H_2O-CH_3]^+$), 150 (83, $[M-C_2H_4O]^+$), 95 (100).

The analogous reaction of **19′** (900 mg) yielded **20′** (600 mg, 61%). IR ($CHCl_3$): 2932, 2863, 1448, 1381, 1366, 929. $^1$H-NMR (300 MHz, $CDCl_3$): 3.19 (*dd*, $^3J$(3,2eq) = 6.1, $^3J$(3,2ax) = 0.5, H–C(3)); 1.73 (*dd*, $^2J$ = 15.1, $^3J$(2eq,3) = 6.1, $H_{eq}$–C(2)); 1.55–1.10 (*m*, 11 H); 1.07 (*s*, $Me_{eq}$–C(5)); 0.96 (*s*, Me–C(1)); 0.92 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 61.5 (*t*, $^1J$(C,D) = 26.1, C(4)); 52.6 (C(3)); 45.1 (C(6)); 44.0 (C(10)); 41.3 (C(2)); 32.8 (C(1)); 32.4 (C(5)); 27.5 ($Me_{eq}$–C(5)); 27.3 (C(8)); 22.3 (C(9)); 22.1 (C(7)); 22.0, 21.5 (*Me*–C(1), $Me_{ax}$–C(5)). EI-MS: 195 (5, $M^{+\cdot}$), 180 (78, $[M-CH_3]^+$), 162 (100, $[M-H_2O-CH_3]^+$), 151 (97, $[M-C_2H_4O]^+$).

*(1*RS*,3*RS*,4*RS*,6*SR*)-3-Iodo-1,5,5-trimethylbicyclo[4.4.0]decane-4-ol Acetate* (=*(2*RS*,3*RS*,4a*RS*,8a*SR*)-Decahydro-3-iodo-1,1,4a-trimethylnaphthalen-2-ol Acetate*; **21**) *and (1*RS*,3*RS*,4*RS*,6*SR*)-3-Iodo-1,5,5-trimethyl(4-$^2$H)bicyclo[4.4.0]decan-4-ol Acetate* (**21′**). Following the procedure of [13], a soln. of **20** (425 mg) in abs. $CH_2Cl_2$ (2 ml) was added to the soln. of $I_2$ (610 mg) and $PPh_3$ (630 g) in abs. $CH_2Cl_2$ (30 ml), and the mixture was stirred at r.t. (15 h). After evaporation, the residue was dissolved in $Ac_2O$ and filtered over a small amount of $SiO_2$. Then abs. pyridine (1 ml) was added and the mixture kept at r.t. (2 h). Usual workup and CC (hexane/AcOEt 30:1) gave **21** (550 mg, 69%). Yellowish oil that crystallized. M.p. 59–61°. IR ($CHCl_3$): 3024, 3016, 2929, 2855, 1727, 1448, 1372, 1248, 1224, 1214, 1101, 1033, 978, 909. $^1$H-NMR (300 MHz, $CDCl_3$): 5.30 (*d*, $^3J$(4,3) = 11.6, H–C(4)); 4.43 (*ddd*, $^3J$(3,2) = 11.6, $^3J$(3,2eq) = 10.0, $^3J$(3,2ax) = 7.9, H–C(3)); 2.36 (*dd*, $^2J$ = 14.5, $^3J$(2eq,3) = 9.8, $H_{eq}$–C(2)); 2.20 (*dd*, $^2J$ = 14.5, $^3J$(2ax,3) = 7.9, $H_{ax}$–C(2)); 2.14 (*s*, COMe); 1.8–1.0 (*m*, 9 H); 1.18 (*s*, $Me_{eq}$–C(5)); 0.93 (*s*, Me–C(1)); 0.89 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 170.2 (*C*OMe); 78.2 (C(4)); 52.2 (C(6)); 48.2 (C(2)); 45.2 (C(10)); 39.0 (C(5)); 36.7 (C(1)); 27.7 (C(3)); 26.9 (C8)); 24.1, 23.7, 23.1 (*Me*–C(1), $Me_{ax}$–C(5), $Me_{eq}$–C(5)); 22.8, 22.0 (C(7), C(9)); 21.3 (CO*Me*). CI-MS: 382 (100, $[M+NH_4]^+$), 322 (10, $[M-C_2H_2O]^+$), 305 (29, $[M-OAc]^+$).

An analogous treatment of **20′** (500 mg) and CC gave **21′** (700 mg, 75%). Amber crystals. M.p. 62–64°. IR ($CHCl_3$): 2969, 2934, 2864, 1733, 1469, 1370, 1252, 1162, 1135, 1048, 1029. $^1$H-NMR (300 MHz, $CDCl_3$): 4.42 (*dd*, $^3J$(3,2eq) = 9.8, $^3J$(3,2ax) = 7.9, H–C(3)); 2.36 (*dd*, $^2J$ = 14.5, $^3J$(2eq,3) = 9.8, $H_{eq}$–C(2)); 2.20 (*dd*, $^2J$ = 14.5, $^3J$(2ax,3) = 7.9, $H_{ax}$–C(2)); 2.14 (*s*, COMe); 1.8–1.0 (*m*, 9 H); 1.18 (*s*, $Me_{eq}$–C(5)); 0.93 (*s*, Me–C(1)); 0.89 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 170.2 (*C*OMe); 77.8 (*t*, $^1J$(C,D) = 23.4, C(4)); 52.2 (C(6)); 48.2 (C(2)); 45.2 (C(10)); 39.0 (C(5)); 36.7 (C(1)); 27.7 (C(3)); 26.9 (C(8)); 24.1, 23.7, 23.1 (*Me*–C(1), $Me_{ax}$–C(5), $Me_{eq}$–C(5)); 22.8, 22.0 (C(7), C(9)); 21.3 (CO*Me*). CI-MS: 383 (100, $[M+NH_4]^+$), 323 (6, $[M-C_2H_2O]^+$), 306 (12, $[M-OAc]^+$).

*(1*RS*,3*SR*,4*RS*,6*SR*)-1,5,5-Trimethylbicyclo[4.4.0]decane-3,4-diol 4-Acetate* (=*(2*RS*,3*SR*,4a*RS*,8a*SR*)-Decahydro-1,1,4a-trimethylnaphthalene-2,3-diol 2-Acetate*; **22**) *and (1*RS*,3*SR*,4*RS*,6*SR*)-1,5,5-Trimethyl(4-$^2$H)bicyclo[4.4.0]decane-3,4-diol 4-Acetate* (**22′**). According to [14], a soln. of **21** (270 mg) in abs. $CH_2Cl_2$ (5 ml) was treated with 40% MeCOOOH in AcOH (0.8 ml) at r.t. (15 h). After workup and CC (hexane/AcOEt 5:1), the less-polar fraction contained the 3$\alpha$,4$\alpha$-diol 3$\alpha$-acetate **23** (25 mg, 13%). The main fraction yielded **22** (85 mg, 45%). Colorless amorphous crystals[11]). M.p. 127–129°. IR ($CHCl_3$): 3597, 3024, 3016, 2937, 2857, 1720, 1464, 1451, 1375, 1260, 1217, 1211, 1124, 1074, 1044, 984, 975, 950, 913. $^1$H-NMR (300 MHz, $CDCl_3$): 4.91 (*d*, $^3J$(4,3) = 2.9, H–C(4)); 4.18 (*ddd*, $^3J$(3,2ax) = 11.4, $^3J$(3,2eq) = 5.2, $^3J$(3,4) = 2.9, H–C(3)); 2.14 (*s*, COMe); 1.86–1.78 (*m*, 1 H); 1.62–1.03 (*m*, 10 H); 0.99 (*s*, $Me_{eq}$–C(5); 0.92 (*s*, Me–C(1)); 0.86 (*s*, $Me_{ax}$–C(19)). $^{13}$C-NMR (150.9 MHz, $CDCl_3$): 172.2 (*C*OMe); 81.1 (C(4)); 65.5 (C(3)); 47.2 (C(6)); 45.0 (C(10)); 43.4 (C(2)); 38.2 (C(5)); 35.1 (C(1)); 27.6 ($Me_{eq}$–C(5)); 27.4 (C(8)); 21.4 (C(9)); 21.3, 21.2 (*Me*–C(1), $Me_{ax}$–C(5)); 21.0 (C(7)); 19.9 (CO*Me*). CI-MS: 272 (100, $[M+NH_4]^+$), 255 (33, $[M+H]^+$), 237 (9), 212 (20, $[M-C_2H_2O]^+$), 195 (6).

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11) TLC of the crude residue showed only one product; acyl migration occurred during CC. Since the target diols **24** and **24′** can be obtained from either isomer, the minor 3$\alpha$,4$\alpha$-diol 3$\alpha$-acetates **23** and **23′** are not described here.

Starting from **21′** (600 mg), the analogous procedure furnished **23′** (45 mg, 11%) and **22′** (205 mg, 49%) as colorless plates[11]). M.p. 136–139° IR ($CHCl_3$): 3598, 3007, 2971, 2936, 2857, 1720, 1464, 1450, 1392, 1371, 1268, 1152, 1100, 1077, 1049, 1026, 1001, 964, 936, 912. $^1$H-NMR (300 MHz, $CDCl_3$): 4.16 (*dd*, $^3J$(2,2ax) = 10.9, $^3J$(3,2eq) = 5.8, H–C(3)); 2.13 (*s*, COMe); 1.86–1.78 (*m*, 1 H); 1.52–1.15 (*m*, 10 H); 0.99 (*s*, $Me_{eq}$–C(5)); 0.91 (*s*, Me–C(1)); 0.85 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 171.9 (*C*OMe); 80.7 (*t*, $^1J$(C,D) = 23.2, C(4)); 65.3 (C(3)); 47.3 (C(6)); 45.0 (C(10)); 43.5 (C(2)); 38.0 (C(5)); 35.1 (C(1)); 27.5 ($Me_{eq}$–C(18)); 27.4 (C(8)); 21.4 (C(9)); 21.3, 21.2 (*Me*–C(1), $Me_{ax}$–C(5)); 21.0 (C(7)); 19.9 (CO*Me*). CI-MS: 273 (100, $[M+NH_4]^+$), 256 (24, $[M+H]^+$), 238 (10), 213 (8, $[M-C_2H_2O]^+$).

*(1*RS*,3*SR*,4*RS*,6*SR*)-1,5,5-Trimethylbicyclo[4.4.0]decane-3,4-diol* (= *(2*RS*,3*SR*,4a*RS*,8a*SR*)-Decahydro-1,1,4a-trimethylnaphthalene-2,3-diol*; **24**) *and (1*RS*,3*SR*,4*RS*,6*SR*)-1,5,5-trimethyl(4-$^2$H)bicyclo[4.4.0]decane-3,4-diol* (**24′**). $LiAlH_4$ (25 mg) was added to a soln. of **22** (38 mg) in abs. THF at 0° and stirred (1 h). Workup and CC (hexane/AcOEt 3:1) afforded **24** (27 mg, 85%). Colorless crystals. M.p. 133–135°. IR ($CHCl_3$): 3566, 3005, 2934, 2855, 1463, 1449, 1384, 1329, 1262, 1237, 1218, 1206, 1191, 114, 1088, 1076, 1030, 986, 953, 932, 912, 900. $^1$H-NMR (300 MHz, $CDCl_3$): 4.05 (*ddd*, $^3J$(3,2ax) = 11.3, $^3J$(3,2eq) = 5.5, $^3J$(3,4) = 2.9, H–C(3)); 3.45 (*d*, $^3J$(4,3) = 2.9, H–C(4)); 2.12–1.86 (*s*, $w_{1/2} \approx 10$, 2 OH); 1.85–1.77 (*m*, $H_{eq}$–C(7)); 1.53–1.39 (*m*, 5 H); 1.37–1.14 (*m*, 5 H); 0.99 (*s*, $Me_{eq}$–C(5)); 0.97 (*s*, Me–C(1)); 0.83 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (150.9 MHz, $CDCl_3$): 79.5 (C(4)); 66.4 (C(3)); 46.0 (C(6)); 45.2 (C(10)); 43.5 (C(2)); 38.3 (C(5)); 35.2 (C(1)); 28.1 ($Me_{eq}$–C(5)); 27.6 (C(8)); 21.6 (C(9)); 21.3 (C(7)); 21.3, 20.0 (*Me*–C(1), $Me_{ax}$–C(5)). CI-MS: 230 (100, $[M+NH_4]^+$).

The analogous procedure with **22′** (140 mg) gave **24′** (106 mg, 91%). Colorless crystals. M.p. 136–138°. IR ($CHCl_3$): 3571, 3006, 2934, 2854, 1463, 1449, 1406, 1384, 1368, 1296, 1256, 1124, 1056, 1022, 999, 985, 950, 904, 658, 608. $^1$H-NMR (300 MHz, $CDCl_3$): 4.04 (*dd*, $^3J$(3,2ax) = 10.5, $^3J$(3,2eq) = 5.2, H–C(3)); 2.38 (*s*, $w_{1/2} \approx 10$, 2 OH); 1.85–1.77 (*m*, $H_{eq}$–C(7)); 1.53–1.39 (*m*, 5 H); 1.37–1.14 (*m*, 5 H); 0.98 (*s*, $Me_{eq}$–C(5)); 0.97 (*s*, Me–C(1)); 0.83 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 78.9 (*t*, $^1J$(C,D) = 22.1, C(4)); 66.2 (C(3)); 45.9 (C(6)); 45.1 (C(10)); 43.4 (C(2)); 38.2 (C(5)); 35.1 (C(1)); 28.0 ($Me_{eq}$–C(5)); 27.5 (C(8)); 21.5 (C(9)); 21.2 (C(7)); 21.1, 19.9 (*Me*–C(1), $Me_{ax}$–C(5)). CI-MS: 231 (100, $[M+NH_4]^+$).

*(1*RS*,3*SR*,4*RS*,6*SR*)-1,5,5-Trimethylbicyclo[4.4.0]decane-3,4-diol 3-(4-Methylbenzenesulfonate)* (= *(2*RS*,3*SR*,4a*RS*,8a*SR*)-Decahydro-1,1,4a-trimethylnaphthalene-2,3-diol 3-(4-Methylbenzenesulfonate)*; **25**) *and (1*RS*,3*SR*,4*RS*,6*SR*)-1,5,5-Trimethyl(4-$^2$H)bicyclo[4.4.0]decane-3,4-diol 3-(4-Methylbenzenesulfonate)* (**25′**). TsCl (46 mg) was added to a soln. of **24** (20 mg) in abs. pyridine (2 ml), and the mixture was kept at r.t. (40 h). Then $H_2O$ was added and the mixture extracted with $Et_2O$. CC (hexane/AcOEt 5:1) gave **25** (32 mg, 93%). White crystals. M.p. 95–97°. IR ($CHCl_3$): 3597, 3025, 3016, 2931, 2867, 1599, 1451, 1359, 1292, 1228, 1189, 1176, 1144, 1097, 1051, 991, 942, 929, 915, 902, 837, 815, 672, 666, 664, 603, 588, 555. $^1$H-NMR (300 MHz, $CDCl_3$): 7.81, 7.35 (*AA′BB′*, *J* = 8.4, arom. H); 4.90 (1 H, *ddd*, $^3J$(3,2ax) = 12.6, $^3J$(3,2eq) = 4.5, $^3J$(3,4) = 2.6, H–C(3)); 3.51 (*d*, $^3J$(4,3) = 2.6, H–C(4)); 2.45 (*s*, *Me*$C_6H_4$); 1.95–1.85 (*s*, $w_{1/2} \approx 4$, OH); 1.84–1.73 (*m*, *t*-like, 2 H); 1.46–1.15 (*m*, 9 H); 0.95 (*s*, $Me_{eq}$–C(5)); 0.89 (*s*, Me–C(1)); 0.79 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 144.7, 134.2 (arom. C); 129.8 (2 C), 127.6 (2 C, arom. CH); 80.1 (C(3)); 77.5 (C(4)); 45.5 (C(6)); 44.7 (C(10)); 40.0 (C(2)); 38.9 (C(5)); 35.5 (C(1)); 27.8 ($Me_{eq}$–C(18)); 27.2 (C(8)); 21.3 (C(9)); 21.5, 21.2, 19.7 (*Me*–C(1), $Me_{ax}$–C(5), *Me*$C_6H_4$); 20.9 (C(7)). CI-MS: 384 (100, $[M+NH_4]^+$), 230 (59, $M+NH_4-TsH]^+$), 212 (72, $[M+NH_4-TsOH]^+$), 195 (17, $[M+H-TsOH]^+$).

Analogous treatment of **24′** (32 mg) gave **25′** (53 mg, 96%). White crystals. M.p. 99–101°. IR ($CHCl_3$): 3598, 2968, 2934, 2867, 1599, 1495, 1463, 1450, 1357, 1307, 1176, 1121, 1098, 1045, 1020, 994, 979, 930, 906, 887, 865, 837, 814, 658, 598, 555. $^1$H-NMR (300 MHz, $CDCl_3$): 7.81, 7.35 (*AA′BB′*, *J* = 8.4, arom. H); 4.90 (*dd*, $^3J$(3,2ax) = 12.6, $^3J$(3,2eq) = 4.5, H–C(3)); 2.46 (*s*, *Me*$C_6H_4$); 1.95–1.85 (*s*, $w_{1/2} \approx 4$, OH); 1.84–1.73 (*m*, *t*-like, 2 H); 1.46–1.15 (*m*, 9 H); 0.95 (*s*, $Me_{eq}$–C(5)); 0.88 (*s*, Me–C(1)); 0.79 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 144.7, 134.2 (arom. C); 129.8 (2 C), 127.6 (2 C, arom. CH); 80.1 (C(3)); 77.1 (*t*, $^1J$(C,D) = 21.9, C(4)); 45.5 (C(6)); 44.7 (C(10)); 40.0 (C(2)); 38.8 (C(5)); 35.5 (C(1)); 27.8 ($Me_{eq}$–C(5)); 27.2 (C(8)); 21.3 (C(9)); 21.6, 21.2, 19.7 (*Me*–C(1), $Me_{ax}$–C(5), *Me*$C_6H_4$); 20.9 (C(7)). CI-MS: 385 (100, $[M+NH_4]^+$), 238 (27), 213 (20, $[M+NH_4-TsOH]^+$), 196 (15, $[M+H-TsOH]^+$).

11. *Reactions of the* (±)-trans-*decalins:* **25** → **17**, **36** *and* **25′** → **36′**, **38**. *(1*RS*,3*RS*,4*RS*,6*SR*)-1,5,5-Trimethyl(3-$^2$H)bicyclo[4.4.0]decan-4-ol* (= *(2*RS*,3*RS*,4a*RS*,8a*SR*)-Decahydro-1,1,4a-trimethyl(3-$^2$H)naphthalen-2-ol*; **38**). To a soln. of **25** (50 mg) in abs. THF (4 ml) was added $LiAlH_4$ (50 mg), and the mixture was stirred at r.t. under $N_2$ (1 h). Workup and CC (hexane/AcOEt 35:1) yielded **17** (23 mg, 86%). Viscous oil.

The analogous treatment of **25′** (47 mg) gave **38** (21 mg, 83%). White amorphous solid. M.p. 66–69°. IR ($CHCl_3$): 3614, 2973, 2929, 2852, 1460, 1383, 1248, 1085, 1006, 954. $^1$H-NMR (600 MHz, $CDCl_3$): 3.22 (*m*, *quint.*-like, $^3J$(4,3eq) ≈ 5, $^3J$(4,D) ≈ 1.5, H–C(4)); 1.80 (*m*, *dq*-like, $^2J$ = 13.5, $H_{eq}$–C(8)); 1.61 (*m*, *t*-like, $w_{1/2} \approx 10$, H–C(3)); 1.58 (*m*, *dq*-like, $^2J$ = 13.5, $H_{eq}$–C(7)); 1.44 (br. *m*, $CH_2$(9)); 1.40 (*dd*, $^2J$ = 13, $^3J$(2eq,3) = 3.5,

$H_{eq}$–C(2)); 1.29 (*m*, *dq*-like, $^2J$ = 13, $H_{eq}$–C(10)); 1.25 (br. *m*, *dt*-like, $^2J$ = 13.5, $H_{ax}$–C(7)); 1.18 (br. *m*, *t*-like, $H_{ax}$–C(2), $H_{ax}$–C(8)); 1.03 (br. *m*, $H_{ax}$–C(10)); 0.96 (*s*, $Me_{eq}$–C(5)); 0.91 (*s*, Me–C(1)); 0.83 (*dd*, $^3J$(6,7ax) = 12.0, $^3J$(6,7eq) = 2.7, H–C(6)); 0.75 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 79.3 (C(4)); 52.6 (C(6)); 45.2 (C(10)); 40.1 (C(2)); 38.7 (C(5)); 34.1 (C(1)); 27.7 ($Me_{eq}$–C(5)); 27.4 (C(7)); 27.2 (*t*, $^1J$(C,D) = 19.5, C(3)); 21.6 (C(9)); 21.5 (C(7)); 19.1 (*Me*–C(1)); 14.9 ($Me_{ax}$–C(5)). EI-MS: 197 (27, $M^{+\bullet}$), 182 (13, $[M - CH_3]^+$), 164 (71, $[M - CH_3 - H_2O]^+$), 137 (64), 83 (100).

*(1*RS,*6*SR*)-1,5,5-Trimethylbicyclo[4.4.0]decan-4-one* (= *(4a*RS,*8a*SR*)-3,4,4a,5,6,7,8,8a-Octahydro-1,1,4a-trimethylnaphthalen-2(1*H*)-one;* **36**) *and (1*RS,*3*RS,*6*SR*)-1,5,5-Trimethyl(3-*$^2$*H)bicyclo[4.4.0]decan-4-one* (**36′**). A soln. of **17** (14 mg) in acetone (2 ml) was treated with 2.7M *Jones* reagent (50 µl) at 0° (5 min). Workup and CC (hexane/AcOEt 30:1) afforded **36** [8a][10] (11.5 mg, 83%). Clear, viscous oil. $^1$H-NMR (300 MHz, $CDCl_3$): 2.71 (*ddd*, $^2J$ = 15.5, $^3J$(3ax,2ax) = 13.5, $^3J$(3ax,2eq) = 6.5, $H_{ax}$–C(3)); 2.30 (*ddd*, $^2J$ = 15.5, $^3J$(3eq,2ax) = 5.2, $^3J$(3eq,2eq) = 2.9, $H_{eq}$–C(3)); 1.83 (*m*, br. *d*-like, 1 H); 1.68 (*ddd*, $^2J$ = 13.3, $^3J$(2eq,3ax) = 6.5, $^3J$(2eq,3eq) = 2.9, $H_{eq}$–C(2)); 1.6–1.2 (*m*, 9 H); 1.11 (*s*, $Me_{eq}$–C(5)); 1.06 (*s*, Me–C(1)); 1.01 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 216.9 (C(4)); 53.5 (C(6)); 47.8 (C(3)); 44.1 (C(10)); 40.8 (C(2)); 35.0 (C(3)); 34.0 (C(1)); 26.9 (C(8)); 25.3 ($Me_{eq}$–C(5)); 22.7 (C(9)); 21.7 (C(7)); 21.4 (*Me*–C(1)); 18.3 ($Me_{ax}$–C(5)). EI-MS: 194 (72, $M^{+\bullet}$), 137 (55), 108 (100).

Analogous oxidation of **38** (14 mg) gave **36′** (12 mg, 87%). Clear, viscous oil. $^1$H-NMR (300 MHz, $CDCl_3$): 2.30 (*m*, *quint.*-like, $^3J$(3,2ax) ≈ 5.2, $^3J$(3,2eq) = 2.9, $^2J$(3,D) ≈ 2.5, H–C(3)); 1.83 (*m*, br. *d*-like, 1 H); 1.68 (*dd*, $^2J$ = 13.5, $^3J$(2eq,3) = 2.9, $H_{eq}$–C(2)); 1.6–1.2 (*m*, 9 H); 1.10 (*s*, $Me_{eq}$–C(5)); 1.06 (*s*, Me–C(1)); 1.00 (*s*, $Me_{ax}$–C(5)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 217.2 (C(4)); 53.5 (C(6)); 47.9 (C(5)); 44.1 (C(10)); 40.7 (C(2)); 34.7 (*t*, $^1J$(C,D) = 19.0, C(3)); 34.0 (C(1)); 26.9 (C(8)); 25.3 ($Me_{ax}$–C(5)); 22.7 (C(9)); 21.7 (C(7)); 21.3 (*Me*–C(1)); 18.4 ($Me_{ax}$–C(5)). EI-MS: 195 (44, $M^{+\bullet}$), 180 (7, $[M - CH_3]^+$), 162 (6, $[M - CH_3 - H_2O]^+$), 137 (36), 108 (100).

*Ketones* **36** *and* **36′** *from Tosylates* **25** *and* **25′**. *a*) A soln. of **25** (5 mg) in abs. pyridine (4 ml) was refluxed (18 h). Then $H_2O$ was added and extracted with $Et_2O$. The residue was purified by TLC (hexane/AcOEt 5:1) to give **36** (4 mg, 87%).

The identical procedure was followed with **25′** (3 mg), but only the undeuterated **36** was isolated, and the expected labelled **36′** could not be detected. Since **36** and **36′** are not separable by GC, the identification was performed by GC/EI-MS, by which the analysis of the total ion current (TIC) exhibited only *m/z* 194 ($M^{+\bullet}$ of **36**), and no trace of the expected *m/z* 195 ($M^{+\bullet}$ of **36′**) could be evidenced. This finding is corroborated by comparison with pure **36′** and its EI-MS that are stored in our GC/MS spectral library[12]).

*b*) A soln. of **25** (4 mg) in abs. toluene (4 ml) was refluxed (18 h). Workup and purification as described in *a*) gave **36** (3.3 mg, 90%).

The identical thermal reaction was performed with **25′** (3 mg) and the product analyzed by GC/MS according to *a*). The only product was **36**, whereas **36′** could not be detected.

*c*) NaOEt (12 mg) was added to a soln. of **25** (11 mg) in abs. THF (2 ml), and the mixture was stirred at r.t. (2 h). Workup and purification as described in *a*) gave **36** (3 mg, 51%). *d*) NaH (80% suspension in oil; 7 mg) was added to a soln. of **25** (8 mg) in abs. THF (2 ml), and the mixture was stirred at r.t. (2 h). Workup and purification as described in *a*) gave **36** (2 mg, 47%).

The identical reactions *c*) and *d*) were performed with **25′** (each 4 mg). GC/MS Analysis of the isolated ketones (each 1 mg, 47%) exhibited the presence of both the undeuterated **36** (*m/z* 194 ($M^{+\bullet}$)) and that of the labeled **36′** (*m/z* 195 ($M^{+\bullet}$)) in the ratio of *ca.* 6:1, as calculated from the relative intensities of the individual TICs.

12. *(±)-Podocarpa-8,11,13-trienes* (*(±)-*trans-*1,2,3,4,4a,9,10,10a-Octahydro-1,1,4a-trimethylphenanthrenes*) **27**–**35** *and* **27′**–**35′**. *(3*RS*)-Podocarpa-8,11,13-trien-3-ol* (= *(2*RS,*4a*RS,*10a*SR*)-1,2,3,4,4a,9,10,10a-Octahydro-1,1,4a-trimethylphenanthren-2-ol*; **27**) *and (3*RS*)-(3-*$^2$*H)Podocarpa-8,11,13-trien-3-ol* (**27′**). To a soln. of **26** [9] (2.74 g) in abs. THF (30 ml), $LiAlH_4$ (1.15 g) was added in portions at 0°, and the mixture was stirred at r.t. (1 h). After workup as described in *Exper. 7*, the residue was dissolved in abs. EtOH (20 ml) and stirred in the presence of 10% Pd/C (1 g) under a slight $H_2$ pressure at r.t. (15 h). Bulb-to-bulb disitillation at 150°/0.02 Torr gave **27** [9b][11] (2.45 g, 88%). Clear oil. $^1$H-NMR (600 MHz, $CDCl_3$): 7.25 (*d*, $^3J$(11,12) = 7.7, H–C(11)); 7.13 (*t*, $^3J$(12,11) = $^3J$(12,13) = 7.7, H–C(12)); 7.09–7.05 (*m*, H–C(13), H–C(14)); 3.32 (*dd*, $^3J$(3,2ax) = 11.4, $^3J$(3,2eq) = 4.7, H–C(3)); 2.97 (*dd*, $^2J$ = 17.1, $^3J$(7eq,6ax) ≈ 6.5, $H_{eq}$–C(7)); 2.89 (*ddd*, $^2J$ = 17.1, $^3J$(7ax,6ax) = 11.5, $^3J$(7ax,6eq) = 7.5, $H_{ax}$–C(7)); 2.33 (*dt*, $^2J$ = 13.1, $^3J$(1eq,2eq) = $^3J$(1eq,2ax) = 3.5, $H_{eq}$–C(1)); 1.91 (br. *m*, *ddt*-like, $H_{eq}$–C(6)); 1.87–1.74 (*m*, $H_{ax}$–C(6), $CH_2$(2)); 1.56 (*dt*, $^2J$ = $^3J$(1ax,2ax) = 13.1, $^3J$(1ax,2eq) = 4.1,

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12) This shows that there is no significant D-exchange under the GC conditions.

$H_{ax}$–C(1)); 1.34 (*dd*, $^3J$(5,6ax) = 12.3, $^3J$(5,6eq) = 2.2, H–C(5)); 1.21 (*s*, Me(17)); 1.09 (*s*, Me(15)); 0.92 (*s*, Me(16)). $^{13}$C-NMR (150.9 MHz, $CDCl_3$): 149.6 (C(9)); 135.3 (C(8)); 129.2 (C(14); 126.0 (C(11)); 125.6, 124.7 (C(12), C(13)); 79.0 (C(3)); 50.0 (C(5)); 39.3 (C(4)); 37.9 (C(10)); 37.2 (C(1)); 30.9 (C(7)); 28.4 (C(15)); 28.3 (C(2)); 25.1 (C(17)); 19.1 (C(6)); 15.6 (C(16)). EI-MS: 244 (29, $M^{+\cdot}$), 229 (31, $[M-CH_3]^+$), 211 (100, $[M-CH_3-H_2O]^+$).

Analogous treatment of **26** (1.02 g) with $LiAlD_4$ (0.5 g) afforded **27′** (916 mg, 88%), after bulb-to-bulb distillation at 150°/0.02 Torr. White crystals. M.p. 84–86°. IR ($CHCl_3$): 3614, 3007, 2969, 2868, 1488, 1456, 1388, 1378, 1248, 1135, 1098, 1066, 1042, 932. $^1$H-NMR (300 MHz, $CDCl_3$): 7.24 (*m*, H–C(11)); 7.13–6.98 (*m*, H–C(12), H–C(13), H–C(14)); 2.94, 2.87 (*AB* of *ABMX*, $CH_2$(7)); 2.33 (*dt*, $^2J$ = 13.0, $^3J$(1eq,2eq) = $^3J$(1eq,2ax) = 3.5, $H_{eq}$–C(1)); 1.91 (br. *m*, $H_{eq}$–C(6)); 1.87–1.72 (*m*, $H_{ax}$–C(6), $CH_2$(2)); 1.56 (*td*, $^2J$(1ax,1eq) = $^3J$(1ax,2ax) = 3.0, $^3J$(1ax,2eq) = 4.1, $H_{ax}$–C(1)); 1.31 (*dd*, $^3J$(5,6ax) = 12.0, $^3J$(5,6eq) = 2.4, H–C(5)); 1.18 (*s*, Me(17)); 1.06 (*s*, Me(15)); 0.89 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 149.6 (C(9)); 135.3 (C(8)); 129.2 (C(14)); 126.0 (C(11)); 125.6, 124.7 (C(12), (C(13)); 78.4 (*t*, $^1J$(C,D) = 21.3, C(3)); 50.0 (C(5)); 39.3 (C(4)); 37.9 (C(10)); 37.2 (C(1)); 30.9 (C(7)); 28.4 (C(15)); 28.3 (C(2)); 25.1 (C(17)); 19.1 (C(6)); 15.6 (C(16)). EI-MS: 245 (31, $M^{+\cdot}$), 230 (33, $[M-CH_3]^+$), 212 (100, $[M-CH_3-H_2O]^+$).

*(3*RS*)-Podocarpa-8,11,13-trien-3-ol Methanesulfonate* (= *(2*R*S,4a*RS*,10a*S*R)-1,2,3,4,4a,9,10,10a-Octahydro-1,1,4a-trimethylphenanthren-2-ol Methanesulfonate*; **28**) *and (3*RS*)-(3-*$^2$*H)Podocarpa-8,11,13-trien-3-ol Methanesulfonate* (**28′**). Reaction of **27** (2.45 g) in abs. pyridine (20 ml) with methanesulfonyl chloride (2 ml) as described in *Exper. 4* gave **28** (1.73 g, 54%), after CC (hexane/AcOEt 30:1 → 15:1). Clear yellowish oil that crystallized after a few days. M.p. 107–109° (from hexane). IR ($CHCl_3$): 3008, 2973, 1489, 1478, 1448, 1356, 1332, 1172, 1043, 971, 958, 942, 917, 882, 843. $^1$H-NMR (300 MHz, $CDCl_3$): 7.23–7.01 (*m*, arom. H); 4.39 (*dd*, $^3J$(3,2ax) = 11.5, $^3J$(3,2eq) = 5.3, H–C(3)); 3.02 (*s*, $MeSO_3$); 2.95, 2.88 (*AB* of *ABMX*, $CH_2$(7)); 2.36 (*dt*, $^2J$ = 13.4, $^3J$(1eq,2eq) = $^3J$(1eq,2ax) = 3.6, $H_{eq}$–C(1)); 2.16–2.05 (*m*, 2 H); 1.91–1.71 (*m*, 2 H); 1.58 (*td*, $^2J$ = $^3J$(1ax,2ax) = 13.4, $^3J$(1ax,2eq) = 3.6, $H_{ax}$–C(1)); 1.41 (*ddd*, $^3J$(5,6ax) = 12.0, $^3J$(5,6eq) = 2.6, $^4J$(5,17) = 0.5, H–C(5)); 1.22 (*d*, $^4J$(17,5) = 0.5, Me(17)); 1.11 (*s*, Me(15)); 0.98 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 148.4 (C(9)); 134.7 (C(8)); 129.0 (C(14)); 125.9 (C(11)); 125.7, 124.3 (C(12), C(13)); 89.9 (C(3)); 50.0 (C(5)); 38.8 ($MeSO_3$); 38.7 (C(4)); 37.3 (C(10)); 36.5 (C(1)); 30.4 (C(7)); 28.3 (C(15)); 25.9 (C(2)); 24.8 (C(17)); 18.9 (C(6)); 16.2 (C(16)). CI-MS: 340 (100, $[M+NH_4]^+$), 227 (85, $[M+H-MsOH]^+$).

Analogous treatment of **27′** (913 mg) with methanesulfonyl chloride (0.8 ml) afforded **28′** (650 mg, 54%). Clear yellowish oil that crystallized after a few days. M.p. 133–135° (from acetone). IR ($CHCl_3$): 3008, 2973, 1489, 1478, 1448, 1392, 1380, 1353, 1332, 1176, 1133, 1088, 1068, 1044, 1023, 970, 912, 849. $^1$H-NMR (300 MHz, $CDCl_3$): 7.23–7.02 (*m*, arom. H); 3.03 (*s*, $MeSO_3$); 2.95, 2.88 (*AB* of *ABMX*, $CH_2$(7)); 2.36 (*dt*, $^2J$ = 13.4, $^3J$(1eq,2eq) = $^3J$(1eq,2ax) = 3.6, $H_{eq}$–C(1)); 2.18–2.08 (*m*, 2 H); 1.91–1.71 (*m*, 2 H); 1.58 (*td*, $^2J$ = $^3J$(ax,2ax) = 13.4, $^3J$(1ax,2eq) = 3.6, $H_{ax}$–C(1)); 1.41 (*ddd*, $^3J$(5,6ax) = 12.0, $^3J$(5,6eq) = 2.6, $^4J$(5,17) = 0.5, H–C(5)); 1.22 (*d*, $^4J$(17,5) = 0.5, Me(17)); 1.11 (*s*, Me(15)); 0.98 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 148.4 (C(9)); 134.7 (C(8)); 129.0 (C(14)); 125.9 (C(11)); 125.6, 124.3 (C(12), C(13)); 89.4 (*t*, $^1J$(C,D) = 22.4, C(3)); 50.0 (C(5)); 38.8 ($MeSO_3$); 38.6 (C(4)); 37.3 (C(10)); 36.5 (C(1)); 30.4 (C(7)); 28.2 C(15)); 25.9 (C(2)); 24.8 (C(17)); 18.8 (C(6)); 16.2 (C(16)). CI-MS: 341 (100, $[M+NH_4]^+$), 228 (85, $[M+H-MsOH]^+$).

*(±)-Podocarpa-2,8,11,13-tetraene* (= *(4a*RS*,10a*RS*)-1,4,4a,9,10,10a-Hexahydro-1,1,4a-trimethylphenanthrene*; **29**) *and (±)-(3-*$^2$*H)-Podocarpa-2,8,11,13-tetraene* (**29′**). The mixture of **28** (1.73 g), LiBr (1.40 g), and $Li_2CO_3$ (1.2 g) in abs. dimethylformamide (20 ml) was refluxed (2 h) and worked up as described in *Exper. 5*. The residue was bulb-to-bulb distilled at 140°/0.03 mbar: **29** [11] (960 mg, 79%). Clear liquid. IR ($CHCl_3$): 3008, 2962, 2840, 1488, 1470, 1448, 1434, 1374, 1362, 1044. $^1$H-NMR (300 MHz, $CDCl_3$): 7.28–7.25 (*m*, 1 arom. H); 7.18–7.01 (*m*, 3 arom. H); 5.60 (*ddd*, $^3J$(2,3) = 10.1, $^3J$(2,1eq) = 6.0, $^3J$(2,1ax) = 1.8, H–C(2)); 5.48 (*dd*, $^3J$(3,2) = 10.1, $^4J$(3,1ax) = 2.7, H–C(3)); 2.89, 2.86 (*AB* of *ABMX*, $CH_2$(7)); 2.53 (*dd*, $^2J$ = 16.8, $^3J$(1eq,2) = 6.0, $H_{eq}$–C(1)); 2.11 (br. *d*, $^2J$ = 16.8, $H_{ax}$–C(1)); 1.89–1.63 (*m*, H–C(5), $CH_2$(6)); 1.25 (*d*, $^4J$(17,5) = 0.8, Me(17)); 1.04 (*s*, Me(15)); 0.99 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 147.9 (C(9)); 138.1 (C(3)); 135.4 (C(8)); 128.9 (C(14)); 126.0 (C(11)); 125.9, 125.2 (C(12), C(13)); 121.9 (C(2)); 48.1 (C(5)); 39.8 (C(1)); 37.0 (C(10)); 35.1 (C(4)); 31.9 (C(15)); 31.2 (C(7)); 25.3 (C(17)); 22.4 (C(16)); 19.9 (C(6)). EI-MS: 226 (8, $M^{+\cdot}$), 211 (10, $[M-CH_3]^+$), 144 (100).

Reaction of **28′** (640 mg) with LiBr (525 mg) and $Li_2CO_3$ (440 mg) in abs. dimethylformamide (15 ml) and distillation as above gave pure **29′** (400 mg, 89%). Clear liquid. IR ($CHCl_3$): 3008, 2962, 2840, 1488, 1470, 1447, 1434, 1386, 1374, 1362, 1051, 1041, 680, 555. $^1$H-NMR (300 MHz, $CDCl_3$): 7.28–7.25 (*m*, 1 arom. H); 7.18–7.01 (*m*, 3 arom. H); 5.59 (*dd*, $^3J$(2,1eq) = 6.0, $^3J$(2,1ax) = 1.5, H–C(2)); 2.89, 2.86 (*AB* of *ABMX*, $CH_2$(7)); 2.53 (*dd*, $^2J$ = 16.8, $^3J$(1eq,2) = 6.0, $H_{eq}$–C(1)); 2.11 (*dd*, $^2J$ = 16.8, $^3J$(1ax,2) = 1.5, $H_{ax}$–C(1)); 1.88–1.62 (*m*, H–C(5), $CH_2$(6)); 1.25 (*d*, $^4J$(17,5) = 0.8, Me(17)); 1.04 (*s*, Me(15)); 0.98 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 147.9

(C(9)); 137.7 (*t*, $^1J$(C,D) = 23.6, C(3)); 135.4 (C(8)); 128.9 (C(14)); 126.0 (C(11)); 125.9, 125.3 (C(12), C(13)); 121.7 (C(2)); 48.0 (C(5)); 39.7 (C(1)); 37.0 (C(10)); 35.0 (C(4)); 31.8 (C(15)); 31.2 (C(7)); 25.3 (C(17)); 22.4 (C(16)); 19.9 (C(6)). EI-MS: 227 (7, $M^{+\bullet}$)), 212 (13, $[M - CH_3]^+$), 144 (100), 129 (41).

*(2*RS,*3*SR*)-2,3-Epoxypodocarpa-8,11,13-triene* (= *(6a*RS,*7a*SR,*8a*RS,*9a*SR*)-5,6,6a,7,7a,8a,9,9a-Octahydro-7,7,9a-trimethylphenanthro[2,3-*b*]oxirene*; **30**) *and (2*RS,*3*SR*)-2,3-Epoxy-(3-$^2$H)podocarpa-8,11,13-triene* (**30′**). A soln. of 1M dimethyldioxirane in acetone [7] (7 ml) was added to **29** (106 mg) in abs. $CH_2Cl_2$ (2 ml) at −30°, and the mixture was stirred at r.t. (15 h). Evaporation and CC of the residue (hexane/AcOEt 30:1) gave **30** (75 mg, 66%). Colorless crystals[13]). M.p. 95–97°. IR ($CHCl_3$): 3007, 2968, 2870, 2842, 1489, 1474, 1436, 1390, 1377, 1366, 1045, 101, 989, 946, 826. $^1$H-NMR (300 MHz, $CDCl_3$): 7.24 - 6.99 (*m*, arom. H); 3.36 (*ddd*, $^3J$(2,1eq) = 6.3, $^3J$(2,3) = 3.8, $^3J$(2,1ax) = 0.5, H–C(2)); 2.88 (*d*, $^3J$(3,2) = 3.8, H–C(3)); 2.83, 2.77 (*AB* of *ABMX*, $CH_2$(7)); 2.57 (*dd*, $^2J$ = 14.8, $^3J$(1eq,2) = 6.3, $H_{eq}$–C(1)); 1.82–1.76 (*m*, $H_{ax}$–C(1), $H_{eq}$–C(6)); 1.65–1.50 (*m*, *ddd*-like, $H_{ax}$–C(6)); 1.42 (*ddd*, $^3J$(5,6ax) = 12.4, $^3J$(5,6eq) = 1.7, $^4J$(5,17) = 1.1, H–C(5)); 1.24 (*d*, $^4J$(17,5) = 1.1, Me(17)), 1.18 (*s*, Me(15)), 1.09 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 146.9 (C(9)); 135.5 (C(8)); 128.8 (C(14)); 126.0 (2 C), 125.4 (C(11), C(12), C(13)); 61.2 (C(3)); 52.8 (C(2)); 43.5 (C(5)); 39.3 (C(1)); 36.8 (C(10)); 33.0 (C(4)); 31.5 (C(7)); 28.0 (C(15)); 27.4 (C(17)); 21.8 (C(16)); 19.4 (C(6)). EI-MS: 242 (28, $M^{+\bullet}$), 227 (100, $M - CH_3]^+$), 209 (55, $[M - H_2O - CH_3]^+$).

The analogous reaction of **29′** (290 mg) yielded **30′** (210 mg, 68%)[13]). Colorless crystals. M.p. 94–96°. IR ($CHCl_3$): 3007, 2968, 2209, 1490, 1412, 1390, 1378, 1366, 1126, 1046, 1009, 928, 874, 555. $^1$H-NMR (300 MHz, $CDCl_3$): 7.24–6.99 (*m*, arom. H); 3.35 (*dd*, $^3J$(2,1eq) = 6.3, $^3J$(2,1ax) = 0.5, H–C(2)); 2.83, 2.77 (*AB* of *ABMX*, $CH_2$(7)); 2.57 (*dd*, $^2J$ = 14.8, $^3J$(1eq,2) = 6.3, $H_{eq}$–C(1)); 1.82–1.75 (*m*, $H_{ax}$–C(1), $H_{eq}$–C(6)); 1.65–1.50 (*m*, *ddd*-like, $H_{ax}$–C(6)); 1.42 (*ddd*, $^3J$(5,6ax) = 12.4, $^3J$(5,6eq) = 1.8, $^4J$(5,17) = 1.1, H–C(5)); 1.24 (*d*, $^4J$(17,5) = 1.1, Me(17)); 1.18 (*s*, Me(15)); 1.09 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 146.9 (C(9)); 135.4 (C(8)); 128.8 (C(14)); 126.0 (2 C), 125.4 (C(11), C(12), C(13)); 60.8 (*t*, $^1J$(C,D) = 26.2, C(3)); 52.6 (C(2)); 43.5 (C(5)); 39.2 (C(1)); 36.7 (C(10)); 32.8 (C(4)); 31.4 (C(7)); 28.0 (C(15)); 27.4 (C(17)); 21.7 (C(16)); 19.3 (C(6)). EI-MS: 243 (39, $M^{+\bullet}$), 228 (100, $[M - CH_3]^+$), 210 (63, $[M - H_2O - CH_3]^+$), 129 (53).

*(2*RS,*3*RS*)-2-Iodopodocarpa-8,11,13-trien-3-ol Acetate* (= *(2*RS,*3*RS,*4a*RS,*10a*SR*)-1,2,3,4,4a,9,10,10a-Octahydro-3-iodo-1,1,4a-trimethylphenanthren-2-ol Acetate*; **31**) *and (2*RS,*3*RS*)-2-Iodo(3-$^2$H)podocarpa-8,11,13-trien-3-ol Acetate* (**31′**). According to [13], a soln. of **30** (25 mg) in abs. $CH_2Cl_2$ (1 ml) was added to the soln. of $I_2$ (29 mg) and $PPh_3$ (30 g) in abs. $CH_2Cl_2$ (5 ml), and the mixture was stirred at r.t. (15 h). After evaporation, the residue was dissolved in $Ac_2O$, the soln. filtered over a small amount of $SiO_2$, and then, abs. pyridine (0.5 ml) was added and the mixture kept at r.t. (2 h). Usual workup and CC (hexane/AcOEt 30:1) gave **31** (36 mg, 85%). Clear colorless crystals. M.p. 169–171°. IR ($CHCl_3$): 3008, 2970, 2945, 2870, 1737, 1490, 1469, 1449, 1434, 1396, 1372, 1324, 1248, 1082, 1034. $^1$H-NMR (300 MHz, $CDCl_3$): 7.16–6.98 (*m*, arom. H); 5.50 (*d*, $^3J$(3,2) = 12.2, H–C(3)); 4.45 (*ddd*, $^3J$(2,3) = 12.2, $^3J$(2,1ax) = 9.9, $^3J$(2,1eq) = 8.4, H–C(2)); 3.04 (*dd*, $^2J$ = 14.3, $^3J$(1ax,2) = 9.9, $H_{ax}$–C(1)); 2.87–2.78 (*m*, $H_{eq}$–C(1), $CH_2$(7)); 2.16 (*s*, COMe); 1.78–1.66 (*m*, H–C(5), $CH_2$(6)); 1.50 (*s*, Me(17)); 1.06 (*s*, Me(15)); 1.00 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 170.3 (*C*OMe); 148.8 (C(9)); 134.0 (C(8)); 128.7 (C(14)); 126.6 (C(11)); 126.4, 125.7 (C(12), C(13)); 77.5 (C(3)); 51.6 (C(1)); 46.2 (C(5)); 40.3 (C(10)); 39.0 (C(4)); 31.0 (C(7)); 30.8 (C(17)); 27.7 (C(2)); 24.3 (C(16)); 23.0 (C(15)); 21.4 (CO*Me*); 17.1 (C(6)). CI-MS: 430 (100, $[M + NH_4]^+$), 370 (7, $[M - C_2H_2O]^+$), 353 (25, $[M + H - AcOH]^+$), 225 (63, $[M + H - AcOH - I]^+$), 130 (100).

An analogous treatment of **30′** (180 mg) and CC gave **31′** (250 mg, 82%). Colorless amorphous crystals. M.p. 157–161°. IR ($CHCl_3$): 2970, 1737, 1490, 1469, 1449, 1370, 1248, 1137, 1090, 1030. $^1$H-NMR (300 MHz, $CDCl_3$): 7.20–6.98 (*m*, arom. H); 4.45 (*t*, $^3J$(2,1ax) = $^3J$(2,1eq) = 9.9, H–C(2)); 3.04 (*dd*, $^2J$ = 4.2, $^3J$(1ax,2) = 9.9, $H_{ax}$–C(1)); 2.93–2.70 (*m*, $H_{eq}$–C(1), $H_2C$(7)); 2.16 (*s*, COMe); 1.78–1.68 (*m*, H-C(5), $CH_2$(6)); 1.50 (*s*, Me(17)); 1.05 (*s*, Me(15)); 1.00 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 170.2 (*C*OMe); 148.7 (C(9)); 133.9 (C(8)); 128.6 (C(14); 126.5 (C(11)); 126.3, 125.6 (C(12), C(13)); 77.1 (*t*, $^1J$(C,D) = 23.5, C(3)); 51.5 (C(1)); 46.1 (C(5)); 40.2 (C(10)); 38.8 (C(4)); 30.8 (C(7)); 30.7 (C(17)); 27.5 (C(2)); 24.2 (C(16)); 22.9 (C(15)); 21.3 (CO*Me*); 20.0 (C(6)). CI-MS: 431 (96, $[M + NH_4]^+$), 371 (5, $[M - C_2H_2O]^+$), 354 (38, $[M + H - AcOH]^+$), 226 (63, $[M + H - AcOH - I]^+$), 131 (100).

*(2*RS,*3*SR*)-Podocarpa-8,11,13-triene-2,3-diol 3-Acetate* (= *(2*RS,*3*SR,*4a*RS,*10a*SR*)-1,2,3,4,4a,9,10,10a-Octahydro-1,1,4a-trimethylphenanthrene-2,3-diol 2-Acetate*; **32**) *and (2*RS,*3*RS*)-(3-$^2$H)Podocarpa-8,11,13-triene-2,3-diol 3-Acetate* (**32′**). A soln. of **31** (320 mg) in abs. $CH_2Cl_2$ (6 ml) was treated with 40% MeCOOOH in

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[13]) The less-polar minor fraction contained the 2*β*,3*β*-epoxy derivative (6%). The compound is not described here.

ACOH (1 ml) at r.t. (15 h) [14]. Workup and CC (hexane/AcOEt 10:1 → 3:1) gave **32** (100 mg, 43%). Brownish oil that crystallized after standing for several days[14]). M.p. 159–162°. IR ($CHCl_3$): 3598, 3008, 2970, 1722, 1489, 1447, 1376, 1248, 1045, 981, 958, 908, 620, 556. $^1$H-NMR (300 MHz, $CDCl_3$): 7.29–7.06 (*m*, arom. H); 4.99 (*d*, $^3J$(3,2) = 2.8, H–C(3)); 4.32 (*ddd*, $^3J$(2,1ax) = 12.2, $^3J$(2,1eq) = 4.3, $^3J$(2,3) = 2.8, H–C(2)); 2.97, 2.94 (*AB* of *ABMX*, $CH_2$(7)); 2.36 (*m*, *dd*-like, $^2J$ = 12.2, $^3J$(1eq,2) = 4.3, $H_{eq}$–C(1)); 2.05 (*s*, COMe); 1.88–1.71 (*m*, $H_{ax}$–C(1), H–C(5), $CH_2$(6)); 1.24 (*d*, $^4J$(17,5) = 0.5, Me(17)); 1.07 (*s*, Me(15)), 0.97 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 172.0 (*C*OMe); 148.8 (C(9)); 134.6 (C(8)); 129.1 (C(14); 125.8 (C(11)); 125.6, 123.9 (C(12), C(13)); 80.4 (C(3)); 66.0 (C(2)); 43.9 (C(5)); 40.2 (C(1)); 38.7 (C(10)); 38.1 (C(4)); 29.7 (C(7)); 27.8 (C(15)); 25.5 (C(17)); 21.6 (C(16)); 20.9 (CO*Me*); 18.1 (C(6)). CI-MS: 320 (100, $[M + NH_4]^+$), 303 (20, $[M + H]^+$), 285 (36, $[M + H - H_2O]^+$), 227 (34, $[M + H - CH_3 - AcOH]^+$), 225 (41, $[M + H - AcOH - H_2O]^+$).

Starting from **31′** (115 mg), the analogous procedure furnished **32′** (40 mg, 47%). White crystalline powder[14]). M.p. 154–157°. IR ($CHCl_3$): 3598, 3008, 2970, 1722, 1489, 1372, 1263, 1172, 1135, 1052, 1027, 936. $^1$H-NMR (300 MHz, $CDCl_3$): 7.29–7.06 (*m*, arom. H); 4.32 (*dd*, $^3J$(2,1ax) = 2.2, $^3J$(2,1eq) = 4.3, H–C(2)); 2.97, 2.94 (*AB* of *ABMX*, $CH_2$(7)); 2.36 (*dd*, $^2J$ = 12.2, $^3J$(1eq,2) = 4.3, $H_{eq}$–C(1)); 2.05 (*s*, COMe); 1.88–1.71 (*m*, $H_{ax}$–C(1), H–C(5), CHC(6)); 1.24 (*d*, $^4J$(17,5) = 0.5, Me(17)); 1.07 (*s*, Me(15)); 0.97 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 172.0 (*C*OMe); 148.8 (C(9)); 134.6 (C(8)); 129.1 (C(14)); 125.9 (C(11)); 125.6, 123.9 (C(12), C(13)); 80.1 (*t*, $^1J$(C,D) = 23.2, C(3)); 66.1 (C(2)); 43.9 (C(5)); 40.1 (C(1)); 38.7 (C(4)); 38.0 (C(10)); 29.7 (C(7)); 27.8 (C(15)); 25.5 (C(17)); 21.6 (C(16)); 20.9 (CO*Me*); 18.1 (C(6)). CI-MS: 321 (100, $[M + NH_4]^+$), 304 (18, $[M + H]^+$), 286 (5, $[M + H - H_2O]^+$), 228 (10, $[M + H - CH_3 - AcOH]^+$), 226 (12, $[M + H - AcOH - H_2O]^+$).

*(2*RS,*3*SR*)-Podocarpa-8,11,13-triene-2,3-diol* (= *(2*RS,*3*SR,*4a*RS,*10a*SR*)-1,2,3,4,4a,9,10,10a-Octahydro-1,1,4a-trimethylphenanthrene-2,3-diol*; **34**) *and (2*RS,*3*SR*)-(3-*$^2$*H)-Podocarpa-8,11,13-triene-2,3-diol* (**34′**). $LiAlH_4$ (40 mg) was added to a soln. of **32** (60 mg) in abs. THF at 0° and stirred (1 h). Workup and CC (hexane/AcOEt 5:1) afforded **34** (39 mg, 76%). White crystals. M.p. 150–154°. IR ($CHCl_3$): 3568, 2966, 1734, 1602, 1489, 1474, 1381, 1249, 1150, 1102, 1038, 990, 943, 921, 884, 822, 619, 556. $^1$H-NMR (300 MHz, $CDCl_3$): 7.26–7.01 (*m*, arom. H); 4.15 (*ddd*, $^3J$(2,1ax) = 12.2, $^3J$(2,1eq) = 4.4, $^3J$(2,3) = 2.9, H–C(2)); 3.50 (*d*, $^3J$(3,2) = 2.9, H–C(3)); 2.97, 2.94 (*AB* of *ABMX*, $CH_2$(7)); 2.28 (*m*, $H_{eq}$–C(1), 2 OH); 1.87–1.68 (*m*, $H_{ax}$–C(1), H–C(5), $CH_2$(6)); 1.21 (*s*, Me(17)); 1.08 (*s*, Me(15)); 0.96 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 148.9 (C(9)); 134.7 (C(8)); 129.0 (C(14)); 125.7 (C(11)); 125.4, 123.9 (C(12), C(13)); 78.7 (C(3)); 66.9 (C(2)); 42.6 (C(5)); 40.0 (C(1)); 38.7 (C(4)); 38.2 (C(10)); 29.9 (C(7)); 28.2 (C(15)); 25.5 (C(17)); 21.6 (C(16)); 18.2 (C(6)). EI-MS: 260 (29, $M^{+\bullet}$), 245 (20, $[M - CH_3]^+$), 227 (100, $[M - CH_3 - H_2O]^+$).

The analogous procedure with **32′** (22 mg) gave **34′** (14 mg, 74%). White crystals. M.p. 147–150°. IR ($CHCl_3$): 3568, 3007, 2967, 1488, 1448, 1380, 1248, 1134, 1052, 1022, 940, 888. $^1$H-NMR (300 MHz, $CDCl_3$): 7.27–7.01 (*m*, arom. H); 4.16 (*dd*, $^3J$(2,1ax) = 12.2, $^3J$(2,1eq) = 4.5, H–C(2)); 2.97, 2.94 (*AB* of *ABMX*, $CH_2$(7)); 2.28 (*dd*, $^2J$ = 12.2, $^3J$(1eq,2) = 4.5, $H_{eq}$–C(1)); 2.11 (br. *s*, $w_{1/2} \approx 5$, OH); 1.87–1.68 (*m*, $H_{ax}$–C(1), H–C(5), $H_2$C(6)); 1.21 (*s*, Me(17)); 1.08 (*s*, Me(15)); 0.96 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 148.9 (C(9)); 134.7 (C(8)); 129.0 (C(14); 125.7 (C(11)); 125.4, 123.9 (C(12), C(13)); 78.2 (*t*, $^1J$(C,D) = 21.9, C(3)); 66.8 (C(2)); 42.6 (C(5)); 40.0 (C(1)); 38.7 (C(4)); 38.1 (C(10)); 29.9 (C(7)); 28.2 (C(15)); 25.5 (C(17)); 21.6 (C(16)); 18.2 (C(6)). EI-MS: 261 (27, $M^{+\bullet}$), 246 (18, $[M - CH_3]^+$), 228 (100, $[M - CH_3 - H_2O]^+$).

*(2*RS,*3*SR*)-Podocarpa-8,11,13-triene-2,3-diol 2-(4-Methylbenzenesulfonate)* (= *(2*RS,*3*SR,*4a*RS,*10a*SR*)-1,2,3,4,4a,9,10,10a-Octahydro-1,1,4a-trimethylphenanthrene-2,3-diol 3-(4-Methylbenzenesulfonate)*; **35**) *and (2*RS,*3*SR*)-(3-*$^2$*H)Podocarpa-8,11,13-triene-2,3-diol 2-(4-Methylbenzenesulfonate)* (**35′**). TsCl (40 mg) was added to a soln. of **34** (15 mg) in abs. pyridine (1 ml), and the mixture was kept at r.t. (40 h). Then $H_2O$ was added and the mixture extracted with $Et_2O$. CC (hexane/AcOEt 10:1) gave **35** (18 mg, 74%). Colorless oil that crystallyzed after several days. M.p. 139–141°. IR ($CHCl_3$): 3608, 2969, 1599, 1490, 1362, 1176, 1098, 1050, 996, 935, 900, 838, 815, 605, 557. $^1$H-NMR (300 MHz, $CDCl_3$): 7.87, 7.40 (*AA′XX′*, *J* = 8.2, arom. H); 7.12–7.00 (*m*, arom. H); 5.03 (*ddd*, $^3J$(2,1ax) = 10.2, $^3J$(2,1eq) = 6.3, $^3J$(2,3) = 2.4, H–C(2)); 3.57 (*d*, $^3J$(3,2) = 2.4, H–C(3)); 2.92, 2.88 (*AB* of *ABMX*, $CH_2$(7)); 2.49 (*s*, *Me*$C_6H_4$); 2.15–2.09 (*m*, $H_{eq}$–C(1), OH); 1.79–1.64 (*m*, $H_{ax}$–C(1), H–C(5), $CH_2$(6)); 1.14 (*s*, Me(17)); 1.06 (*s*, Me(15)); 0.93 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 148.1 (C(9)); 144.9 (arom. C); 134.6 (C(8)), 134.2 (arom. C); 129.9 (2 arom. CH); 129.0 (C(14)); 127.7 (2 arom. CH); 125.7 (C(11)); 125.4, 123.9 (C(12), C(13)); 80.5 (C(2)); 76.6 (C(3)); 42.6 (C(5)); 39.0 (C(10)); 38.7 (C(4)); 36.8 (C(1)); 29.6 (C(7)); 28.0 (C(15)); 25.3 (C(17)); 21.6, 21.5 (C(16), *Me*$C_6H_4$); 18.0 (C(6)). CI-MS: 432 (95, $[M + NH_4]^+$), 260 (100).

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[14]) Acyl migration was not observed (→ 2,3-diol 2-acetates **33** and **33′**).

Analogous treatment of **34′** (14 mg) gave **35′** (18 mg, 74%). White crystals. M.p. 136–141°. IR ($CHCl_3$): 3605, 3008, 2969, 1599, 1490, 1448, 1395, 1364, 1308, 1176, 1098, 1049, 999, 935, 900, 867, 832, 815, 602, 557. $^1$H-NMR (300 MHz, $CDCl_3$): 7.87, 7.40 (*AA′XX′*, $J$ = 8.2, arom. H); 7.12–7.00 (*m*, arom. H); 5.02 (*dd*, $^3J$(2,1ax) = 10.4, $^3J$(2,1eq) = 6.5, H–C(2)); 2.92, 2.88 (*AB* of *ABMX*, $CH_2$(7)); 2.48 (*s*, *Me*$C_6H_4$); 2.15–2.09 (*m*, $H_{eq}$–C(1), OH); 1.81–1.58 (*m*, $H_{ax}$–C(1), H–C(5), $CH_2$(6)); 1.12 (*s*, Me(17)); 1.05 (*s*, Me(15)); 0.93 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 148.1 (C(9)); 144.9 (arom. C); 134.6 (C(8)), 134.2 (arom. C); 129.9 (2 arom. CH); 129.0 (C(14)); 127.7 (2 arom. CH); 125.8 (C(11)); 125.6, 123.5 (C(12), C(13)); 80.5 (C(2)); 76.1 (*t*, $^1J$(C,D) = 22.2, C(3)); 42.2 (C(5)); 39.0 (C(10)); 38.7 (C(4)); 36.8 (C(1)); 29.6 (C(7)); 28.0 (C(15)); 25.3 (C(17)); 21.6, 21.5 (C(16), *Me*$C_6H_4$); 18.0 (C(6)). CI-MS: 433 (99, $[M + NH_4]^+$), 260 (100).

13. *Reactions of the (±)-Podocarpanes:* **35** → **27**, **37** *and* **35′** → **37′**, **39**). *(2*RS,*3*SR*)-(2-*$^2$*H)-Podocarpa-8,11,13-trien-3-ol* (= *(2*RS,*3*RS,*4a*RS,*10a*SR*)-1,2,3,4,4a,9,10,10a-Octahydro-1,1,4a-trimethyl(3-*$^2$*H)phenanthren-2-ol*; **39**). To a soln. of **35** (20 mg) in abs. THF (2 ml) was added $LiAlH_4$ (18 mg), and the mixture was stirred at r.t. under $N_2$ (1 h). Workup and CC (hexane/AcOEt 10:1) yielded **27** (10 mg, 85%). Clear oil.

The analogous treatment of **35′** (20 mg) gave **39** (10.5 mg, 89%). White amorphous powder. M.p. 95–97°. IR ($CHCl_3$): 3614, 3007, 2970, 1488, 1378, 1090, 1071, 1030, 938. $^1$H-NMR (600 MHz, $CDCl_3$): 7.24 (*d*, $^3J$(11,12) = 7.6, H–C(11)); 7.12 (*t*, $^3J$(12,11) = $^3J$(12,13) = 7.6, H–C(12)); 7.09–7.03 (*m*, H–C(13), H–C(14)); 3.30 (br. *d*, $^3J$(3,2eq) ≈ 4, H–C(3)); 2.97 (*dd*, $^2J$ = 17.1, $^3J$(7eq,6ax) = 6.5, $H_{eq}$–C(7)); 2.89 (*ddd*, $^2J$ = 17.1, $^3J$(7ax,6ax) = 11.5, $^3J$(7ax,6eq) = 7.5, $H_{ax}$–C(7)); 2.32 (*dd*, $^2J$ = 13.1, $^3J$(1eq,2) = 3.5, $H_{eq}$–C(1)); 1.91 (br. *m*, *ddt*-like, $H_{eq}$–C(6)); 1.81 (br. *s*, $w_{1/2}$ ≈ 12, H–C(2)); 1.76 (*dddd*, $^2J$ = 13.0, $^3J$(6ax,5) = 12.2, $^3J$(6ax,7ax) = 11.5, $^3J$(6ax,7eq) = 6.5, $H_{ax}$–C(6)); 1.55 (br. *d*, $^2J$ = 13.1, $H_{ax}$–C(1)); 1.33 (*dd*, $^3J$(5,6ax) = 12.2, $^3J$(5,6eq) = 2.2, H–C(5)); 1.20 (*s*, Me(17)); 1.08 (*s*, Me(15)); 0.90 (*s*, Me(16)). $^{13}$C-NMR (150.9 MHz, $CDCl_3$): 149.6 (C(9)); 135.2 (C(8)); 129.2 (C(14)); 126.0 (C(11)); 125.6, 124.7 (C(12), C(13)); 78.9 (C(3)); 50.0 (C(5)); 39.3 (C(4)); 37.9 (C(10)); 37.1 (C(1)); 30.9 (C(7)); 28.4 (C(15)); 27.9 (*t*, $^1J$(C,D) = 19.2, C(2)); 25.1 (C(17)); 19.0 (C(6)); 15.6 (C(16)). EI-MS: 245 (27, $M^{+\cdot}$), 230 (25, $[M - CH_3]^+$), 212 (100, $[M - CH_3 - H_2O]^+$).

*(±)-Podocarpa-8,11,13-trien-3-one* (= *(4a*RS,*10a*SR*)-3,4,4a,9,10,10a-Hexahydro-1,1,4a-trimethylphenanthren-2(1*H*)-one*; **37**) *and (2*RS*)-(2-*$^2$*H)Podocarpa-8,11,13-trien-3-one* (**37′**). A soln. of **27** (15 mg) in acetone (1 ml) was treated with 2.7M *Jones* reagent (50 µl) at 0° (10 min). Workup and CC (hexane/AcOEt 30:1) afforded **37** [9] (13 mg, 87%). White crystals. M.p. 88–91°. $^1$H-NMR (300 MHz, $CDCl_3$): 7.27–7.04 (*m*, arom. H); 2.95, 2.91 (*AB* of *ABMX*, $CH_2$(7)); 2.71 (*ddd*, $^2J$ = 15.6, $^3J$(2ax,1ax) = 10.0, $^3J$(2ax,1eq) = 7.4, $H_{ax}$–C(2)); 2.59 (*ddd*, $^2J$ = 15.6, $^3J$(2eq,1ax) = 7.5, $^3J$(2eq,1eq) = 4.1, $H_{eq}$–C(2)); 2.49 (*ddd*, $^2J$ = 13.1, $^3J$(1eq,2ax) = 7.4, $^3J$(1eq,2eq) = 4.1 $H_{eq}$–C(1)); 2.01–1.76 (*m*, $H_{ax}$–C(1), H–C(5), $CH_2$(6)); 1.30 (*d*, $^4J$(17,5) = 0.6, Me(17)); 1.17 (*s*, Me(15); 1.15 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 217.2 (C(3)); 147.3 (C(9)); 134.9 129.1 (C(14)); 126.1 (C(11)); 125.8, 125.4 (C(12), C(13)); 50.6 (C(5)); 47.4 (C(4)); 37.5 (C(1)); 37.4 (C(10)); 34.6 (C(2)); 30.8 (C(7)); 26.9 (C(15)); 24.7 (C(17)); 21.1 (C(16)); 20.2 (C(6)). EI-MS: 242 (49, $M^{+\cdot}$), 227 (36, $[M - CH_3]^+$), 185 (100), 143 (65), 129 (83).

Analogous oxidation of **39** (10 mg) gave **37′** (8.5 mg, 86%). White crystals M.p. 90–93°. IR ($CHCl_3$): 2972, 1699, 1490, 1458, 1386, 1248, 1110, 1042. $^1$H-NMR (300 MHz, $CDCl_3$): 7.27–7.04 (*m*, arom. H); 2.95, 2.91 (*AB* of *ABMX*, $CH_2$(7)); 2.57 (*m*, $w_{1/2}$ ≈ 15, $H_{eq}$–C(2)); 2.49 (*dd*, $^2J$ = 13.2, $^3J$(1eq,2eq) = 4.1 $H_{eq}$–C(1)); 2.01–1.76 (*m*, $H_{ax}$–C(1), H–C(5), $CH_2$(6)); 1.30 (*d*, $^4J$(20,5) = 0.6, Me(17)); 1.17 (*s*, Me(15)); 1.15 (*s*, Me(16)). $^{13}$C-NMR (75.4 MHz, $CDCl_3$): 217.2 (C(3)); 147.3 (C(9)); 134.9 (C(8)); 129.1 (C(14)); 126.1 (C(11)); 125.8, 125.4 (C(12), C(13)); 50.6 (C(5)); 47.4 (C(4)); 37.5 (C(1)); 37.4 (C(10)); 34.3 (*t*, $^1J$(C,D) = 19.5, C(2)); 30.8 (C(7)); 26.9 (C(15)); 24.7 (C(17)); 21.1 (C(16); 20.2 (C(6)). EI-MS: 243 (64, $M^{+\cdot}$), 228 (47, $[M - CH_3]^+$), 186 (71), 185 (73), 143 (66), 129 (100).

*Ketones* **37** *and* **37′** *from Tosylates* **35** *and* **35′**. *a*) A soln. of **35** (3 mg) in abs. pyridine (4 ml) was refluxed (18 h). Then $H_2O$ was added and the mixture extracted with $Et_2O$. The residue was purified by TLC (hexane/AcOEt 4:1): **37** (1.5 mg, 86%).

*b*) A soln. of **35** (3 mg) in abs. toluene (4 ml) was refluxed (18 h). Workup and purification as described in *a*) gave **37** (1.6 mg, 91%).

*c*) NaOEt (4 mg) was added to a soln. of **35** (3 mg) in abs. THF (2 ml), and the mixture was stirred at r.t. (2 h). Workup and purification as described in *a*) gave **37** (1 mg, 57%).

*d*) NaH (80% suspension in oil; 4 mg) was added to a soln. of **35** (3 mg) in abs. THF (2 ml), and the mixture was stirred at r.t. (2 h). Workup and purification as described in *a*) gave **37** (1 mg, 57%).

The identical procedures *a*)–*d*) were followed with **35′**, but only the undeuterated ketone **37** was isolated, whereas the expected **37′** could not be detected. Since **37** and **37′** are not separable by GC, the identification was performed by GC/EI-MS where the analysis of the TIC only exhibited *m/z* 242 ($M^{+\cdot}$ of **37**), and no trace of the

expected *m/z* 243 ($M^{+\cdot}$ of **37′**) could be evidenced. This finding is corroborated by comparison with pure **37′** and its EI-MS that are stored in our GC/MS spectral library[12]).

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