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The synthesis of Ambrox®-like compounds starting from (+)-larixol

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Abstract—The oxidation of the (3-hydroxy-3-methyl-4-pentenyl)-side chain at C(9) of some labdanic diterpenoids with potassium permanganate was investigated. Triols, ketones, or cyclic enol ethers are the main reaction products, strongly influenced by the substituent at C(8). Further degradation of the methyl ketones by the Baeyer–Villiger reaction and modification of the exocyclic 8(17) double bond lead to suitable intermediates, which have been transformed into Ambrox®-like compounds. Synthetic routes using palladium catalyzed elimination or isomerization of allylic acetates, followed by ozonolysis have been developed as well for shortening of the side chain of (+)-larixol. Products from both routes have been cyclized to 6α-hydroxy Ambrox®. This compound was used as the key intermediate for the synthesis of several other Ambrox®-like compounds of which some showed pleasant odour properties.

1. Introduction

Labdanes form a large group of diterpenes, characterized by a 4,4,10-trimethyl substituted *trans*-decalin system, with a β-orientated substituted side chain at C(9).[1] Labdane diterpenoids are easily available from Nature and they have been used frequently as starting material for the synthesis of other 4,4,10-trimethyl substituted decalins.[2] The synthesis of (−)-Ambrox® and other flavour compounds from (−)-sclareol[3] has been studied extensively. Larixol (**1**) and larixyl acetate are also easily available from Nature,[4] but have been used to a much lesser extent as starting materials in synthesis. However, oxidation of the C(9) side chain of these labdanes also may provide suitable synthons for the synthesis of Ambrox®-like compounds. For this purpose the side chain of larixol (**1**) has to be shortened to a two carbon moiety and the exocyclic 8(17) methylene group has to be modified to enable the construction of the cyclic ether that is characteristic for Ambrox®-type molecules.

The side chain of labdanes may contain various functional groups, but the labdanic terpenoids used in this research all have the generally occuring (3-hydroxy-3-methyl-4-pentenyl)-side chain at C(9) (Scheme 1). Several studies to oxidize this side chain have been reported in literature for larixol (**1**) and manool,[5–11] but many use expensive, environmentally suspect oxidants, are irreproducible, or give rise to experimental difficulties during work-up. Also some special oxidation procedures, which have been developed for sclareol (**6**),[12–16] do not proceed in the same way for larixol (**1**) due to differences in the functional groups at C(8). The C(8) hydroxyl group of sclareol (**6**) participates in reaction intermediates of the oxidation, while such participation is not possible in larixol (**1**), its acetate (**2**) and in *epi*-manool (**3**). Furthermore the presence of an exocyclic double bond at C(8) in the latter three compounds may cause selectivity problems, and this may be also the case with the hydroxyl group at C(6) in **1** and **4**.

So there is still a need for a general selective good yield procedure for the degradation of the labdane side chain and for this purpose a modification of the method of Ogino et al.[17] using solid potassium permanganate[18] in the presence of a phase-transfer catalyst was investigated for the oxidation of the labdanes **1**–**7**, aiming at an optimum yield for methyl ketones.[9] An obvious way to achieve further breakdown of methyl ketones into a functionalized two carbon moiety is the Baeyer–Villiger oxidation and this reaction was investigated for methyl ketone **11** and for its C(6) acetate **12** and *tert*-butyldimethylsilyl (TBDMS) ether **25**. Pd catalysed isomerization or elimination, followed by ozonolysis can provide for a short route to break down the side chain in labdanes as well. Both routes lead to intermediates which are suitable for cyclization to 6α-hydroxy Ambrox® **39**. This compound can be considered as a key intermediate in the syntheses of other Ambrox®-like compounds as depicted in Scheme 1.

2. Results and discussion

Besides the labdanes larixol (**1**) and C(13)-*epi*-manool (**3**), the oleoresin of the larch turpentine mainly consists of

Keywords: labdanes; larixol; potassium permanganate oxidation; Baeyer–Villiger oxidation; 6α-hydroxy Ambrox®; Ambrox®-like compounds.

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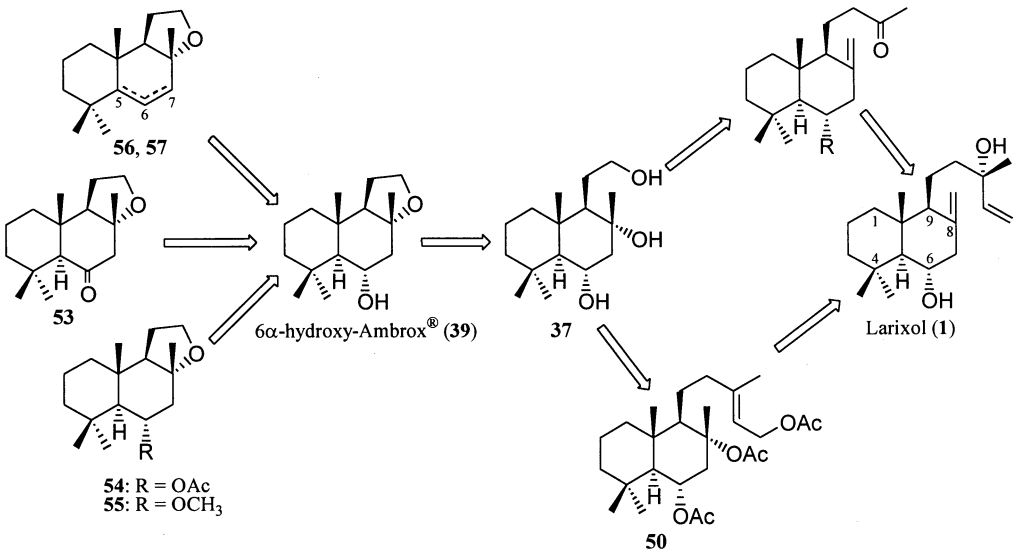


Scheme 1.

larixyl acetate (**2**).[10,19,20] To facilitate purification, the acetate is hydrolyzed first to larixol (**1**), which can be obtained in pure form via crystallization from cyclohexane. The most apolar compound in the residual mother liquor is (+)-*epi*-manool (**3**),[21,22] which can be isolated easily by chromatography. Compound **4** was obtained from larixol (**1**) in 64% overall yield after epoxidation of the exocyclic double bond with oxone and reduction of the epoxide using lithium aluminum hydride ($LiAlH_4$) and its structure was fully determined (vide infra in Scheme 5).[23] The corresponding acetate **5** was obtained after treatment of compound **4** with acetic anhydride in pyridine. Compound **7**[24] was synthesized from larixol (**1**) in 73% overall yield by oxidation of the C(6)-hydroxyl group with pyridinium chlorochromate (PCC) to the C(6)-ketone, which was transformed into the conjugated ketone **7** via base catalyzed isomerization of the exocyclic 8(17) double bond using methanolic sodium methoxide. The same C(6)-ketone can also be obtained by Swern oxidation of larixol (**1**), followed by isomerization.

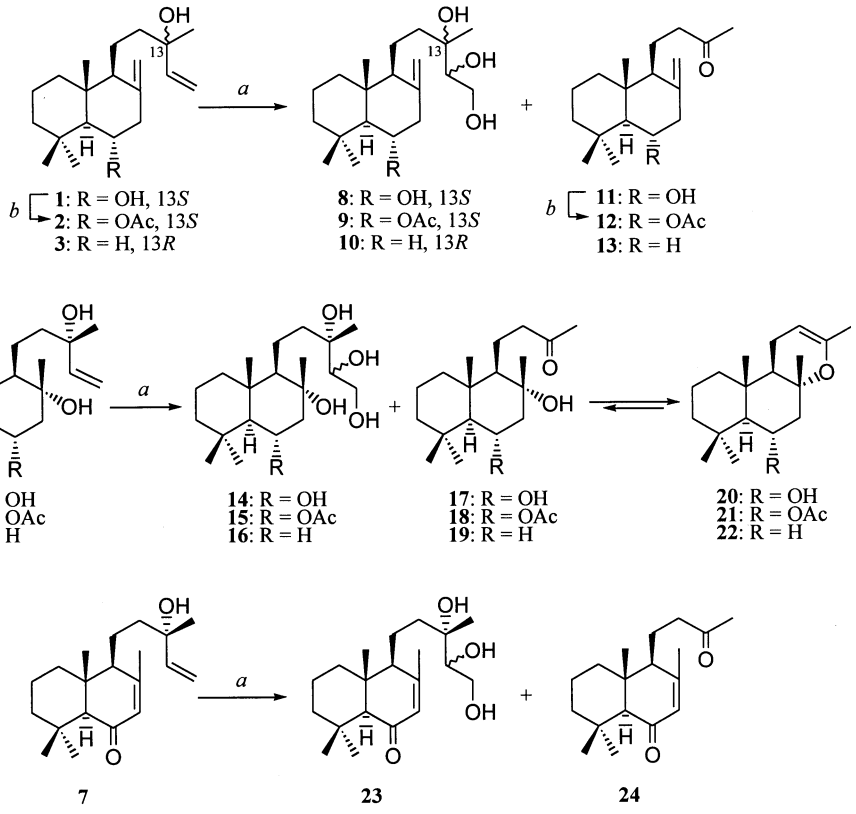
The oxidation of compounds **1**–**7** was investigated using two standard methods with 1.5 or 3.0 equiv. of potassium permanganate respectively, at 0°C, and the results are summarized in Table 1. In all cases mixtures of triols and methyl ketones were obtained (Scheme 2), but it became clear that generally good yields of the desired methyl ketones could be obtained when 3.0 equiv. of potassium permanganate were used. The ratio between the two products was slightly pH dependent with alkaline conditions giving higher yields of the triols.[25,26] Longer reaction times, higher temperature or more equivalents of oxidant gave no improvement of the yield of methyl ketones and in the labdanes **1**–**3** products rising from oxidation of the exocyclic methylene group were found.[10] For substrate **7** the use of 3 equiv. of potassium permanganate did not show a significant difference in product ratio, but when this reaction was carried out at *room temperature*, the methyl ketone **24** is obtained as main product in 68% isolated yield.

The influence of the substituent on C(8) is also clear. When an exocyclic double bond is present at C(8) a reasonable selective oxidation of the double bond in the side chain can be achieved to give the methyl ketones **11**–**13** in good yields. When a hydroxyl group is present at C(8), this group has a strong tendency to react with the methyl ketone in the side chain, and the cyclic enol ethers **20**–**22** are isolated as the main products in high yield. A further breakdown in a *separate* reaction with another 3.0 equiv. of $KMnO_4$ could not be achieved. Decomposition of these enol ethers was observed during longer chromatographic

Table 1. Potassium permanganate oxidation of labdanes using 1.5 and 3.0 equiv., respectively, at 0°C

Substrate	Products on oxidation with 1.5 equiv. $KMnO_4$			Products on oxidation with 3.0 equiv. $KMnO_4$		
	Triol (%)[a]	Methyl ketone (%)[a]	Enol ether (%)[a]	Triol (%)[a]	Methyl ketone (%)[a]	Enol ether (%)[a]
1	**8** (38)	**11** (45)		**8** (–)[b]	**11** (68)	
2	**9** (26)	**12** (48)		**9** (–)[b]	**12** (72)	
3	**10** (24)	**13** (48)		**10** (–)[b]	**13** (67)	
4	**14** (–)[b]	**17** (–)[b]	**20** (47)	**14** (–)[b]	**17** (–)[b]	**20** (74)
5	**15** (–)[b]	**18** (–)[b]	**21** (48)	**15** (–)[b]	**18** (–)[b]	**21** (90)
6[31]	**16** (25)	**19** (6)	**22** (51)	**16** (–)[b]	**19** (–)[b]	**22** (86)
7	**23** (56)	**24** (8)		**23** (56)	**24** (11)	

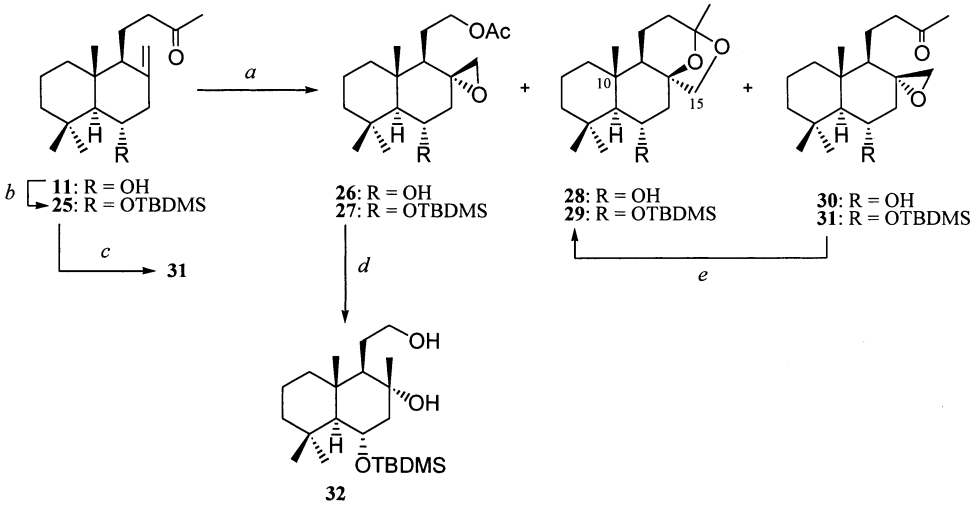
[a] Isolated pure yields.
[b] Not isolated, maximum yield <5%.



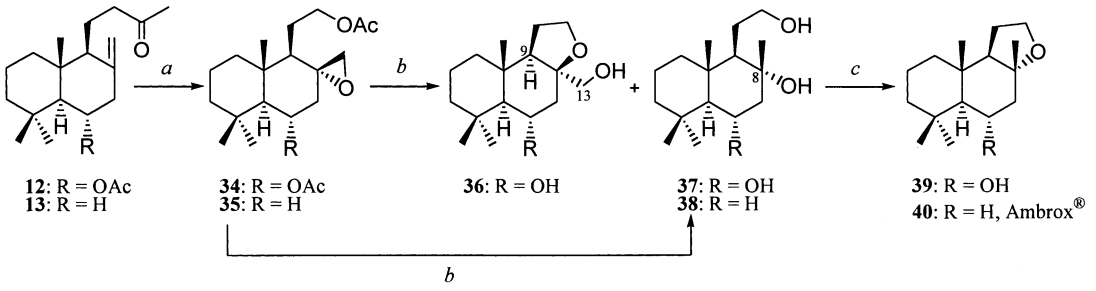
Scheme 2. *Reagents and conditions*: (a) $KMnO_4$, for details see Table 1; (b) Ac_2O, CH_2Cl_2, py, DMAP, 91%.

procedures or upon standing, so in preparative procedures it is advisable to use them immediately for further transformations without purification. Sonication[27] accelerated the oxidation appreciably, i.e. a shortening of the reaction time from 14 to 2 h. However, the yield and product composition was not affected. Presumably, sonication promotes the decomposition of the cyclic manganate ester which is responsible for the formation of the products.[28] The *periodate–permanganate* system for the oxidation of olefinic double bonds[29,30] was also investigated but it did not improve the yields of the methyl ketones.

Further breakdown of the methyl ketones into a functionalized two carbon moiety using the Baeyer–Villiger oxidation[32] was investigated for methyl ketone **11**, its C(6) acetate **12** and its C(6) TBDMS ether **25**. When methyl ketone **11** was treated with 10 equiv. of *meta*-chloroperbenzoic acid (*m*-CPBA) during 10 days acetal **28** was obtained in 50% yield and the expected epoxy acetate **26**



Scheme 3. *Reagents and conditions*: (a) for R=OH: *m*-CPBA (2 equiv.), CH_2Cl_2, 83%, **26**:**28**:**30**=3:4:1; for R=OTBDMS: *m*-CPBA (2.5 equiv.), CH_2Cl_2, 85%, **27**:**29**:**31**=2:2:5; (b) TBDMSiCl, DMF, imidazole, 60°C, 87%; (c) MMPP, CH_2Cl_2, 60%; (d) $LiAlH_4$, THF, 0°C to rt, 62%; (e) spontaneously upon standing.



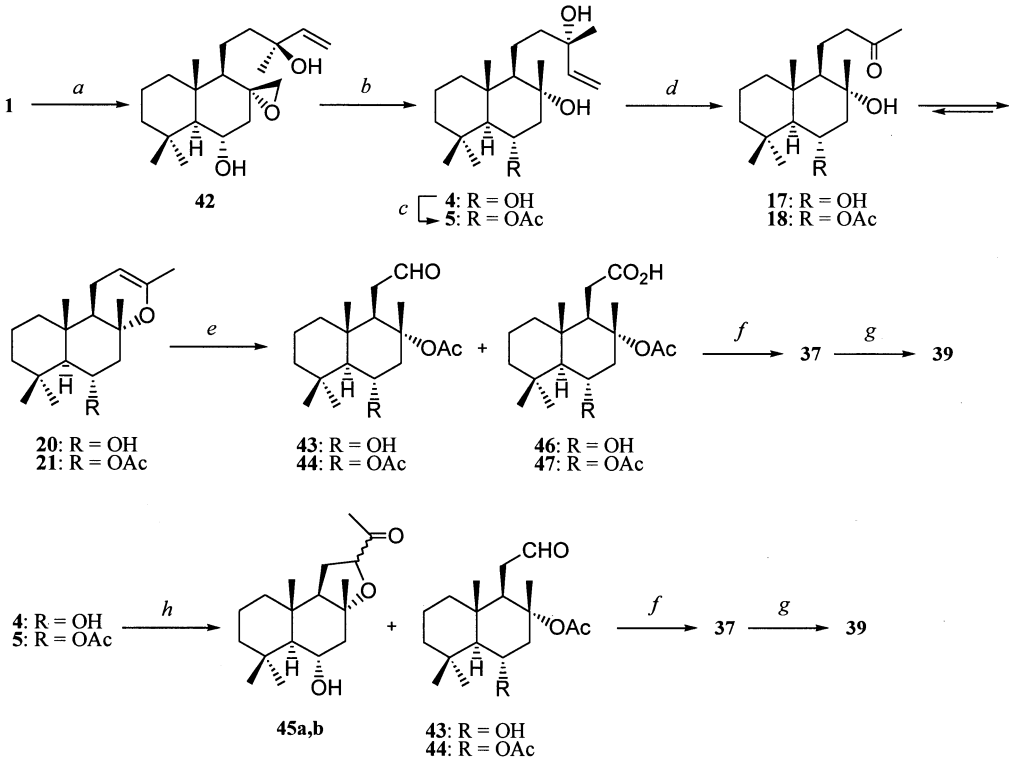
Scheme 4. *Reagents and conditions*: (a) for R=OAc: *m*-CPBA, CH_2Cl_2, 84%; for R=H: see literature data[34]; (b) for R=OH, OAc: $LiAlH_4$, THF, 0°C to rt, 95%, **36**:**35**=1:8.5; for R=H: see literature data[34]; (c) for R=OH: *p*-TsOH, CH_3NO_2, 64%.

was formed in only 35% yield. Treatment of **11** with just 2 equiv. of *m*-CPBA again gave rise to **28** and **26** in 30 and 40% yield, respectively and epoxide **30** was found as a minor byproduct (12%) (Scheme 3).

The structure of compound **28** was elucidated by $^1H,^1H$-NOESY-NMR and $^1H,^1H$-COSY-NMR, whereby no nOe is observed between H(15) and the protons of the C(10)-methyl group. Apparently epoxidation of the double bond is faster than the Baeyer–Villiger oxidation of the methyl ketone and a subsequent acid catalyzed reaction of the carbonyl group with the epoxide than gives the acetal **28**. Baeyer–Villiger oxidation of the TBDMS protected compound **25** with *m*-CPBA gave again a mixture, with the desired epoxy acetate **27** as the minor product. Epoxide **31** was obtained in almost 80% yield as the major product after flash column chromatography, as was established by ^1H NMR. However already during the ^{13}C NMR identification of **31** in $CDCl_3$, acetal **29** was formed and upon standing a conversion of **31** into **29** was also observed.

In an attempt to obtain **27** in a better yield the oxidation was also carried out with magnesium monoperoxyphthalate hexahydrate[33] (MMPP) in stead of *m*-CPBA, but this reagent epoxidized only the exocyclic double bond to give compound **31**, and left the methyl ketone unaffected. On the other hand when acetate **12** was treated with *m*-CPBA compound **34** was obtained in a good yield of 84% together with 11% of compound **33**, in which only the exocyclic double bond is epoxidized (Scheme 4).

The epoxy acetates **26**, **27** and **34** were treated with lithium aluminum hydride ($LiAlH_4$) with the aim to introduce the desired tertiairy hydroxyl group at C(8), and to reduce the acetates to hydroxyl groups as well. However, the reduction of the epoxy acetates **26** and **34** both gave the cyclic ether **36**



Scheme 5. *Reagents and conditions*: (a) oxone, acetone, H_2O, CH_2Cl_2, [18]crown-6, $NaHCO_3$, 0°C, 68%; (b) $LiAlH_4$, THF, 0°C to rt, 94%; (c) Ac_2O, CH_2Cl_2, py, DMAP, 91%; (d) $KMnO_4$, BTEACl, CH_2Cl_2, 0°C to rt, 70–85%; (e) Jones, acetone, 50%; (f) $LiAlH_4$, THF, 0°C to rt, 94%; (g) *p*-TsOH, CH_3NO_2, 64%; (h) for R=OH: cat. OsO_4, $NaIO_4$, THF, 80–90%, **45a**,**b**:**43**=1:2.2; for R=OAc: cat. OsO_4, $NaIO_4$, THF, 72%.

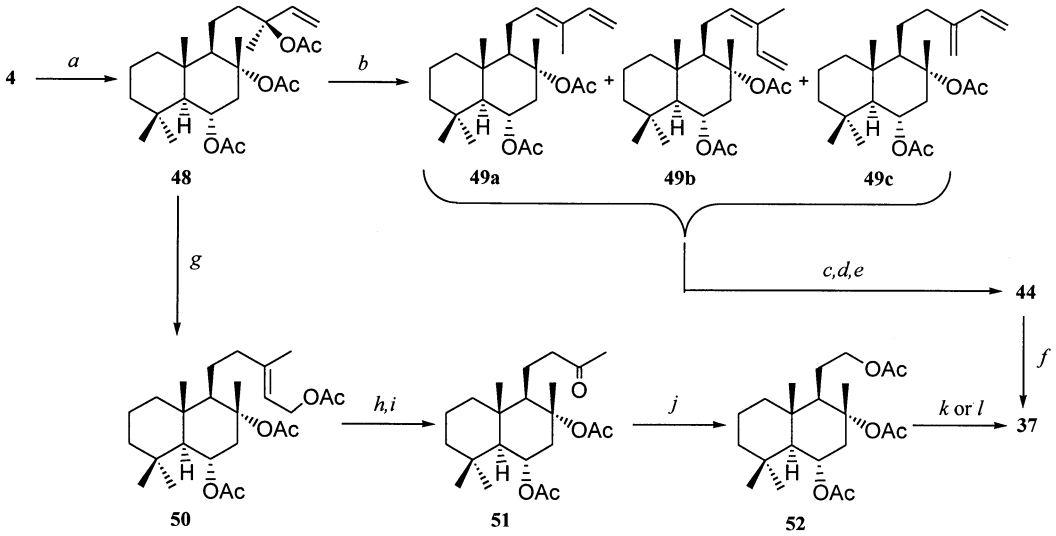
as the main product and the desired triol **37** could be isolated only as a minor product. Obviously the acetate group in the side chain was reduced first, followed by attack of the alkoxide on the epoxide to give the cyclic ether **36**. Its configuration was determined by $^{1}H,^{1}H$-NOESY-NMR, whereby a clear nOe was observed between H(13) and H(9). Reduction of epoxy acetate **27** gave **32** as the sole product in a reasonable 62% yield (Scheme 3). Cyclization of **37** was achieved by stirring in nitromethane in the presence of *p*-toluenesulfonic acid (*p*-TsOH) and gave **39** in 64% yield.

When the results depicted in Schemes 3 and 4 are compared with each other and with a similar reaction sequence of methyl ketone **13**, derived from manool, it can be concluded that the C(6) substituent in larixol (**1**) and its derivatives has a definitive but rather unpredictable influence on the course and yields of the reactions involved. Treatment of methyl ketone **13** with two equivalents of *m*-CPBA effected a clean conversion into the epoxy acetate **35** by successive epoxidation and Baeyer–Villiger reaction. Reduction of this epoxy acetate with $LiAlH_4$ afforded the diol **38** in 72% yield.[34] The related compounds **11** and **25** gave mixtures in the Baeyer–Villiger reaction but the same reaction with acetate **12** gave a high yield of the desired epoxy diacetate **34**. However, the reduction of epoxide **34** proceeded in the wrong way and gave the desired triol **37** in only 10% yield. Although incidental transformations proceeded in good yield, no overall high yield conversion of **11** into key intermediate **39** could be achieved and therefore other routes were investigated.

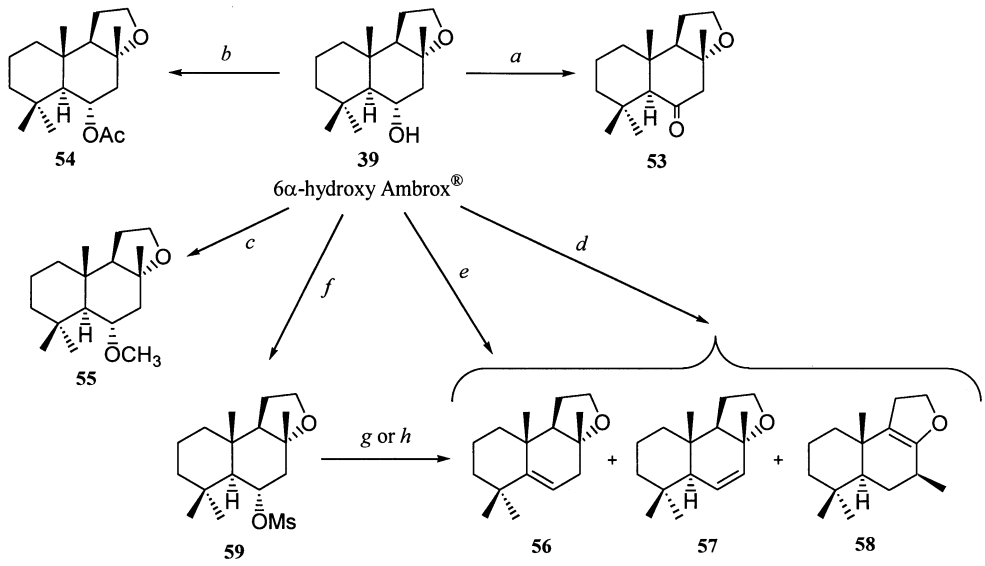
The major difficulties in the former route were connected with the lack of selectivity in the Baeyer–Villiger oxidation of the 3-oxo-butyl side chain and in the reduction of the resulting epoxy acetate. A new route was investigated in which these transformations could be avoided and therefore the exocyclic 8(17) double bond in larixol (**1**) was converted first into a methyl group and a hydroxyl group at C(8). This was performed by epoxidation of this double bond with oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) which proved to be the oxidant of choice compared with *m*-CPBA because its selectivity for the 8(17) exocyclic double bond was much better. Over-epoxidation to give the 8(17), 14(15)-diepoxide **41** was observed in 19%. Epoxide **42** was reduced with $LiAlH_4$ to give the triol **4**[23] which proceeded in good yield and without the competitive formation of cyclic ethers as seen before in Scheme 4. The C(6)-hydroxyl group in **4** could be protected selectively as its acetate **5**, and **4** and **5** were both oxidized with a catalytic amount of osmium tetroxide (OsO_4) and an excess of sodium metaperiodate ($NaIO_4$) (Scheme 5). This oxidation gave the aldehydes **43** and **44** respectively, as the major products along with some side products, of which two were identified as the epimers **45a** and **b**. A high ratio of $NaIO_4/OsO_4$ favoured cleavage to the aldehyde above rearrangement to methyl ketones **45a** and **b**.[35]

Some other routes starting from **4** were also investigated (Scheme 5). Oxidation of **4** or **5** with potassium permanganate ($KMnO_4$)[17] has been mentioned before and leads to formation of the enol ethers **20** and **21**. Attempts to cleave the double bond in these enol ethers by a second oxidation with $KMnO_4$ were unsuccesful, but Jones' oxidation[36] immediately followed by reduction of the resulting mixture of aldehydes and acids gave triol **37** in 50% yield, based on the enol ethers. Various other oxidation procedures were also applied to these enol ethers, but did not lead to improvements.[37] The aldehydes **43** and **44** isolated from the osmylation reactions, both gave triol **37** in 94% yield upon reduction with $LiAlH_4$.

Elimination or rearrangement of allylic acetates in the side chain of larixol or its derivatives followed by ozonolysis also could provide for an easy access to compounds with a two or four carbon moiety at C(9) and this approach was investigated as well. The acetylation of the secondary and both tertiary hydroxyl groups in **4** could be achieved with acetyl chloride in *N*,*N*-dimethylaniline to give the triacetate **48** (Scheme 6). When **48** was treated with a catalytic amount



Scheme 6. *Reagents and conditions*: (a) AcCl, *N*,*N*-dimethylaniline, 80%; (b) $Pd(OAc)_2$, $CaCO_3$, PPh_3, dioxane, Δ, 94%, **49a**:**b**:**c**=4:2:3; (c) O_3, MeOH/CH_2Cl_2 3:1, −78°C; (d) $NaBH_4$, −78°C; (e) NaOMe, MeOH, 67%; (f) $LiAlH_4$, THF, 0°C to rt, 87%; (g) $PdCl_2(CH_3CN)_2$, THF, 98%; (h) O_3, CH_2Cl_2/ MeOH 1:1, −78°C; (i) PPh_3, −78°C, 95%; (j) *m*-CPBA, CH_2Cl_2, 83%; (k) $LiAlH_4$, THF, 0°C to rt, 85%; (l) NaOMe, MeOH, 85%.



Scheme 7. *Reagents and conditions*: (a) $H_2Cr_2O_7$, acetone, 91%; (b) Ac_2O, CH_2Cl_2, py, DMAP, 94%; (c) NaH, MeI, DMF, 100°C, 95%; (d) *p*-TsOH, benzene, Δ, 80%, **56**:**57**:**58**=2:1:1; (e) $SOCl_2$, py, 0°C to rt, 57%; (f) MsCl, 0°C to rt, 92%; (g) LiBr, Li_2CO_3, DMF, 120°C, 71%; (h) MgI_2, toluene, 67%.

(1 mol%) of palladium acetate[3j,38c] in the presence of triphenylphosphine at 100°C, a mixture of unsaturated acetates **49a**, **b** and **c** in a ratio of 4:2:3, determined with ^{1}H NMR, was obtained in over 90% yield. Ozonolysis of this mixture afforded aldehyde **44**, which was reduced and saponified to give triol **37** in 67% yield starting from the mixture of dienes.

In a second variant triacetate **48** was isomerized in quantitative yield to the allylic acetate **50**[38] (Scheme 6). Ozonolysis of the double bond gave the methyl ketone **51**, which was transformed into triacetate **52** by a Baeyer–Villiger oxidation, now in good yield (83%). Exhaustive reduction of **52** with $LiAlH_4$ gave triol **37** in 85% yield. This triol was also obtained in the same yield from the triacetate by saponification using sodium methoxide in methanol.

When the results of the different approaches for the conversion of larixol (**1**) into 6α-hydroxy Ambrox® (**39**) are compared, it can be seen that the best yield is obtained by the route described in Scheme 5, using the poisonous OsO_4. Although the second route described in Scheme 6 needs two steps more, the overall yield of **39** is comparable and environmentally safe chemicals are used. Furthermore, the intermediates are all formed in high yield, which avoids difficult purification procedures, so in our opinion this is the route of choice.

6α-Hydroxy Ambrox® (**39**) was used as the key intermediate for the preparation of some Ambrox®-like compounds (Scheme 7). Treatment of **39** with Jones' reagent in acetone afforded ketone **53** in 91% yield. Conversion of **39** into its acetate **54** was achieved by acetic anhydride in 94% yield, and the reaction of the alkoxide of **39** with methyl iodide gave the methyl ether **55** in 95% yield. When **39** was treated with *p*-toluenesulfonic acid in benzene under Dean Stark conditions a non-separable mixture of three compounds **56**, **57** and **58** was formed in a ratio of 2:1:1, determined with ^{1}H NMR and GC experiments. This pleasant smelling mixture was analysed on a GC-MS apparatus and on a GC-sniff apparatus, and all three compounds had a pleasant smell, with the Δ^5-alkene **56** as the most attractive one. The structure of alkene **56** was deduced from the NMR spectrum and from its MS spectrum, which showed a clear retro Diels–Alder reaction. Moreover, its structure was proven by an independent synthesis (vide infra). Compound **57** showed two vinylic protons which coupled with each other, strongly indicating the proposed structure, which is additionally supported by the MS spectrum. The third product most likely has a rearranged skeleton, but further investigations are required to determine the precise structure.

The Δ^5-alkene **56** was produced in a more selective way in 57% yield by treating **39** with thionyl chloride in pyridine, but this approach was not compatible with the preservation of its pleasant odour. Conversion of **39** to mesylate **59** was achieved by methanesulfonyl chloride in pyridine in a 92% yield, and *syn* elimination of this mesylate by treatment with magnesium iodide in toluene afforded the Δ^5-alkene **56** in 67% yield, with preservation of its pleasant smell. This compound also was obtained in 71% yield from the same mesylate **59** by treatment with lithium bromide and lithium carbonate in *N*,*N*-dimethyl formamide at 120°C. Several attempts were undertaken to achieve a selective synthesis of the Δ^6-alkene, but all met with moderate success.

None of the Ambrox®-like compounds **39**, **53**[39,40]–**55** showed the typical ambergris fragrance properties, only the Δ^5- and the Δ^6-alkenes **56** and **57**, respectively, and **58** had a pleasant smell.

3. Experimental

3.1. General and instrumentation[41]

3.1.1. (+)-(1*S*,4*S*,4a*R*,8a*S*)-4-((3*S*)-3-Hydroxy-3-methyl-4-pentenyl)-4a,8,8-trimethyl-3-methylenedecahydro-1-naphthalenol (larixol (1)). The oleoresin of the larch

turpentine (250 g), purchased from Carl Roth GmbH and Co. (Karlsruhe, Germany), was dissolved in ether (600 mL), and washed with a 2% aqueous solution of KOH (400 mL). The organic layer was evaporated and the yellow residue was dissolved in EtOH (300 mL) and hydrolyzed with a 4 M aqueous solution of KOH (200 mL) by refluxing it for 3 h. The mixture was cooled to room temperature and acidified with a 4 M aqueous solution of HCl. Extraction with ether, followed by usual work up gave the crude larixol as a dark yellow oil. Crystallization from cyclohexane gave pure larixol (**1**) (108 g). Mp 102–103°C (lit.[10a]: 103–104°C); $[\alpha]_D$=+53.0 (*c* 2.1) (lit.[10a]: +50.4); IR (KBr) ν_{max} 3466, 3083, 2928, 1741, 1727, 1374, 1249, 1047 cm^{-1}; ^1H NMR δ 0.64 (s, 3H), 0.91 (s, 3H), 1.12 (s, 3H), 1.22 (s, 3H), 1.09–1.84 (m, 14H), 1.98 (t, *J*=11.6 Hz, 1H), 2.32 (dd, *J*=4.8, 12.1 Hz, 1H), 3.76 (dt, *J*=4.9, 10.7 Hz, 1H), 4.60 (d, *J*=1.4 Hz, 1H), 4.89 (d, *J*=1.4 Hz, 1H), 5.05 (dd, *J*=2.7, 10.7 Hz, 1H), 5.20 (dd, *J*=10.7, 17.4 Hz, 1H), 5.91 (dd, *J*=10.7, 17.4 Hz, 1H); ^{13}C NMR δ 16.0 (q), 18.0 (t), 19.1 (t), 22.3 (q), 27.6 (q), 33.8 (s), 36.6 (q), 39.2 (t), 39.5 (s), 41.3 (t), 43.7 (t), 49.1 (t), 56.4 (d), 60.5 (d), 71.6 (d), 73.5 (s), 108.4 (t), 111.6 (t), 145.2 (d), 145.5 (s); HRMS: (M^+−18), found 288.2449. $C_{20}H_{32}O$ requires 288.2449; MS *m/e* (%) 288 [(M^+−18), 79], 273 (59), 270 (58), 255 (70), 153 (100), 135 (100), 121 (41), 109 (78), 95 (45); Anal. found C, 78.10; H, 11.28%. $C_{20}H_{34}O_2$ requires C, 78.38; H, 11.18%.

3.1.2. (+)-(1*S*,4*S*,4a*R*,8a*S*)-4-((3*S*)-3-Hydroxy-3-methyl-4-pentenyl)-4a,8,8-trimethyl-3-methylenedecahydro-1-naphthalenyl acetate (larixyl acetate (2)). To a solution of larixol (**1a**) (5.0 g; 16.34 mmol) in pyridine (150 mL) was added acetic anhydride (5 mL; 5.44 g; 53.2 mmol) and 4-*N*,*N*-dimethylaminopyridine (50 mg; 0.40 mmol). The reaction mixture was stirred for 1 h, then poured into an ice cold aqueous 4 M solution of HCl, and worked up with ethyl acetate, to give the crude larixyl acetate as a yellow oil. Purification by flash column chromatography on silica gel with PE/EA 4:1 as eluent gave first **(+)-(1*S*)-1-(2-((1*S*,4*S*,4a*S*,8a*R*)-4-(acetyloxy)-5,5,8a-trimethyl-2-methylenedecahydro-1-naphthalenyl)ethyl)-1-methyl-2-propenyl acetate (larixyl diacetate)** (0.58 g; 1.47 mmol; 9%) as a white solid. Mp 115–116.5°C (lit.[21a] 117°C); $[\alpha]_D$=+46.6 (*c* 2.2) (lit.[21a]: +36.0); IR (KBr) ν_{max} 2937, 2895, 1728, 1257, 1243, 1023 cm^{-1}; ^1H NMR δ 0.72 (s, 3H), 0.85 (s, 3H), 0.99 (s, 3H), 1.47 (s, 3H), 1.01–1.95 (m, 13H), 2.02 (s, 3H), 2.04 (s, 3H), 2.57 (dd, *J*=5.1, 12.2 Hz, 1H), 4.61 (d, *J*=1.3 Hz, 1H), 4.91 (d, *J*=1.3 Hz, 1H), 4.97 (dd, *J*=4.5, 11.0 Hz, 1H), 5.08 (s, 1H), 5.14 (d, *J*=5.1 Hz, 1H), 5.95 (d, *J*=10.9, 17.7 Hz, 1H); ^{13}C NMR δ 15.9 (q), 17.6 (t), 19.0 (t), 21.9 (q), 22.2 (q), 22.4 (q), 23.5 (q), 33.5 (s), 36.1 (q), 39.0 (t), 39.1 (t), 39.8 (s), 43.4 (t), 44.3 (t), 56.2 (d), 57.5 (d), 73.1 (d), 83.2 (s), 109.4 (t), 113.1 (t), 141.8 (d), 144.2 (s), 169.9 (s) 170.1 (s); HRMS: (M^++1), found 391.2833. $C_{24}H_{39}O_4$ requires 391.2848; MS *m/e* (%) 391 [(M^++1), 1], 331 (5), 289 (4), 273 (6), 272 (21), 271 (100), 270 (4), 269 (5), 203 (3), 101 (3), 61 (12); Anal. found C, 74.14; H, 9.88%. $C_{24}H_{38}O_4$ requires C, 73.80; H, 9.81%.

Further elution gave larixyl acetate (**2**) (5.07 g; 14.54 mmol; 89%) as a white solid. Mp 78–79°C (lit.[21a]: 82°C); $[\alpha]_D$=+45.2 (*c* 2.4) (lit.[21a]: +67.0); IR (KBr) ν_{max} 3526, 3086, 2931, 2868, 2851, 1767, 1737, 1668, 1369, 1245, 1172 cm^{-1}; ^1H NMR δ 0.70 (s, 3H), 0.83 (s, 3H), 0.97 (s, 3H), 1.21 (s, 3H), 1.02–1.81 (m, 15H), 1.99 (s, 3H), 2.64 (dd, *J*=5.1, 12.2 Hz, 1H), 4.62 (d, *J*=1.3 Hz, 1H), 4.90 (d, *J*=1.3 Hz, 1H), 5.01 (dd, *J*=1.4, 10.7 Hz, 1H), 5.16 (dd, *J*=1.3, 17.4 Hz, 1H), 5.86 (dd, *J*=10.7, 17.4 Hz, 1H); ^{13}C NMR δ 16.0 (q), 18.0 (t), 19.0 (t), 22.0 (q), 22.4 (q), 27.7 (q), 33.5 (s), 36.2 (q), 39.1 (t), 39.8 (s), 41.3 (t), 43.5 (t), 44.2 (t), 56.4 (d), 57.5 (d), 73.3 (d), 73.5 (s) 109.5 (t), 111.7 (t), 144.3 (s), 145.2 (d), 170.1 (s); HRMS: (M^+−60), found 288.2451. $C_{20}H_{32}O$ requires 288.2449; MS *m/e* (%) 288 [(M^+−60), 22], 270 (66), 255 (80), 187 (33), 153 (100), 123 (43), 105 (35), 95 (36), 73 (40), 43 (39); Anal. found C, 75.38; H, 10.39%. $C_{22}H_{36}O_3$ requires C, 75.81; H, 10.41%.

3.1.3. (+)-(3*R*)-5-((1*S*,4a*S*,8a*S*)-5,5,8a-Trimethyl-2-methylenedecahydro-1-naphthalenyl)-3-methyl-1-penten-3-ol (*epi*-manool (3)). 13-*Epi*-manool (**3**) was isolated from the mother liquor left after crystallization of larixol (**1a**) by flash column chromatography on silica gel (eluent PE/EA 15:1) as a very thick light yellow oil, (lit.[21a]: mp 35–38°C). $[\alpha]_D$=+44.6 (*c* 2.6) (lit.[21a]: +48.0); IR (liquid film) ν_{max} 3444, 3082, 2925, 1715, 1645, 1386, 1367, 1120 cm^{-1}; ^1H NMR δ 0.61 (s, 3H), 0.73 (s, 3H), 0.80 (s, 3H), 1.20 (s, 3H), 0.85–2.20 (m, 16H), 2.31 (dd, *J*=4.2, 12.2 Hz, 1H), 4.44 (d, *J*=1.5 Hz, 1H), 4.74 (d, *J*=1.5 Hz, 1H), 4.79 (dd, *J*=1.4, 10.7 Hz, 1H), 5.13 (dd, *J*=1.3, 17.3 Hz, 1H), 5.84 (dd, *J*=10.7, 17.3 Hz, 1H); ^{13}C NMR δ 14.4 (q), 17.7 (t), 19.4 (t), 21.7 (q), 24.4 (t), 27.6 (q), 33.5 (s), 33.6 (q), 38.4 (t), 39.1 (t), 39.9 (s), 41.4 (t), 42.2 (t), 55.6 (d), 57.3 (d), 73.6 (s), 106.5 (t), 111.6 (t), 145.3 (d), 148.7 (s); HRMS: M^+, found 290.2612. $C_{20}H_{34}O$ requires 290.2610; MS *m/e* (%) 290 (M^+, 1), 272 (42), 257 (63), 137 (100), 123 (36), 109 (33), 107 (30), 95 (51), 93 (35), 81 (56), 69 (37).

3.1.4. (+)-(1*S*,3*R*,4*R*,4a*S*,8a*S*)-4-((3*S*)-3-Hydroxy-3-methyl-4-pentenyl)-3,4a,8,8-tetramethyldecahydro-1,3-naphthalenediol (4). Epoxide **42** (5.5 g; 17.08 mmol) was added in small portions at 0°C into a stirred suspension of $LiAlH_4$ (1.3 g; 34.21 mmol) in freshly distilled THF (100 mL). After stirring overnight at room temperature the mixture was treated carefully with ethyl acetate (50 mL), and diluted with an 1 M aqueous solution of HCl (200 mL). The aqueous layer was extracted with ethyl acetate and worked up as usual. The residue was recrystallized from EA/CH_2Cl_2 1:1 to give compound **4** as white crystals (5.2 g; 16.05 mmol; 94%). Mp 158–159°C; $[\alpha]_D$=+43.4 (*c* 1.3, EtOH); IR (KBr) ν_{max} 3427, 2923, 2542, 2474, 1457, 1388 cm^{-1}; ^1H NMR ($CDCl_3$/CD_3OD) δ 0.72 (s, 3H), 0.90 (s, 3H), 1.08 (s, 3H), 1.11 (s, 3H), 1.18 (s, 3H), 1.04–1.48 (m, 13H), 2.00 (dd, *J*=3.8, 11.9 Hz, 1H), 3.26 (br s, 3H), 3.70 (dt, *J*=3.8, 10.7 Hz, 1H), 4.99 (dd, *J*=1.5, 10.7 Hz, 1H), 5.13 (dd, *J*=1.5, 17.4 Hz, 1H), 5.77 (dd, *J*=10.7, 17.4 Hz, 1H); ^{13}C NMR ($CDCl_3$/CD_3OD) δ 15.9 (q), 17.8 (t), 18.7 (t), 21.5 (q), 24.7 (q), 28.6 (q), 33.3 (s), 35.9 (q), 39.2 (s), 39.4 (t), 43.5 (t), 44.3 (t), 51.1 (d), 53.3 (t), 60.7 (d), 68.3 (d), 73.9 (s), 74.0 (s), 111.6 (t), 144.1 (d); HRMS: (M^+−18), found 306.2560. $C_{20}H_{34}O_2$ requires 306.2559; MS *m/e* (%) 306 [(M^+−18), 1], 292 (6), 191 (53), 187 (56), 150 (53), 123 (81), 109 (72), 87 (100), 43 (99); Anal. found C,

73.71; H, 11.37%. $C_{20}H_{36}O_3$ requires C, 74.02; H, 11.18%.

3.1.5. (+)-(1*S*,3*R*,4*R*,4a*S*,8a*S*)-3-Hydroxy-4-((3*S*)-3-hydroxy-3-methyl-4-pentenyl)-3,4a,8,8-tetramethyl-decahydro-1-naphthalenyl acetate (5). A solution of 6α-hydroxy **4** (1.5 g; 4.63 mmol) in CH_2Cl_2 (10 mL) and pyridine (8 mL) was treated with acetic anhydride (1.75 mL; 1.90 g; 18.6 mmol) and DMAP (25 mg; 0.20 mmol) and stirred at 0°C. After stirring for 150 min the mixture was poured into an ice cold aqueous 4 M solution of HCl, and worked up with ethyl acetate. Flash column chromatography (eluent PE/EA 3:1) of the residue gave compound **5** (1.54 g; 4.21 mmol; 91%) as white crystals. Mp 126–128°C; $[\alpha]_D$=+52.9 (*c* 2.1); IR (KBr) ν_{max} 3423, 2924, 2869, 1727, 1716, 1469, 1266, 1239 cm^{-1}; ^1H NMR δ 0.85 (s, 3H), 0.86 (s, 3H), 1.02 (s, 3H), 1.26 (s, 6H), 1.30–1.84 (m, 14H), 2.04 (s, 3H), 2.07 (dd, *J*=3.9, 11.7 Hz, 1H), 2.54 (br s, 2H), 5.07 (dd, *J*=3.3, 10.8 Hz, 1H), 5.23 (dd, *J*=1.4, 17.2 Hz, 1H), 5.87 (dd, *J*=10.8, 17.2 Hz, 1H); ^{13}C NMR δ 16.2 (q), 18.0 (t), 19.0 (t), 22.0 (2×q), 25.6 (q), 29.2 (q), 33.3 (s), 36.1 (q), 39.5 (t), 39.7 (s), 43.5 (t), 44.3 (t), 50.0 (t), 58.4 (d), 61.0 (d), 70.9 (d), 74.1 (s), 74.2 (s), 112.0 (t), 144.9 (d), 170.3 (s); HRMS: (M^+−18), found 348.2669. $C_{22}H_{36}O_3$ requires 348.2664; MS *m/e* (%) 348 [(M^+−18), 2], 288 (44), 191 (48), 190 (81), 121 (43), 109 (50), 95 (50), 81 (50), 71 (44), 69 (48), 43 (100); Anal. found C, 72.44; H, 10.69%. $C_{22}H_{38}O_4$ requires C, 72.09; H, 10.45%.

3.1.6. (+)-(4*S*,4a*R*,8a*S*)-4-((3*S*)-3-Hydroxy-3-methyl-4-pentenyl)-3,4a,8,8-tetramethyl-4a,5,6,7,8,8a-hexahydro-1(4*H*)-naphthalenone (7). To a stirred solution of larixol (**1**) (2.5 g; 8.18 mmol) in CH_2Cl_2 (60 mL) was added 3 Å molecular sieves (2.0 g) followed by pyridinium chlorochromate (PCC) (2.63 g; 12.25 mmol) and 10 drops of acetic acid. After 1 h the mixture was filtered over silica gel 60H and flushed with ethyl acetate. Purification of the crude product by flash column chromatography (PE/EA 3:1) gave **(+)-(4*S*,4a*R*,8a*S*)-4-((3*S*)-3-hydroxy-3-methyl-4-pentenyl)-4a,8,8-trimethyl-3-methyleneoctahydro-1(2*H*)-naphthalenone** (2.35 g; 7.75 mmol; 95%) as a colourless oil. $[\alpha]_D$=+74.6 (*c* 3.0); IR (liquid film) ν_{max} 3467, 2930, 1715, 1652, 1464, 1293, 1233 cm^{-1}; ^1H NMR δ 0.63 (s, 3H), 0.96 (s, 3H), 1.17 (s, 3H), 1.28 (s, 3H), 1.14–1.86 (m, 15H), 4.68 (d, *J*=1.1 Hz, 1H), 4.85 (d, *J*=1.1 Hz, 1H), 5.06 (dd, *J*=1.3, 10.7 Hz, 1H), 5.20 (dd, *J*=1.3, 17.2 Hz, 1H), 5.91 (dd, *J*=10.7, 17.2 Hz, 1H); ^{13}C NMR δ 15.8 (q), 18.2 (t), 18.9 (t), 21.6 (q), 27.9 (q), 32.6 (s), 32.8 (q), 38.9 (t), 41.1 (t), 41.4 (s), 42.7 (t), 55.9 (t), 57.3 (d), 66.4 (d), 73.4 (s), 110.1 (t), 111.9 (t), 143.4 (s), 145.1 (d), 208.2 (s); HRMS: M^+, found 304.2400. $C_{20}H_{32}O_2$ requires 304.2402; MS *m/e* (%) 304 (M^+, 4), 287 (23), 286 (100), 258 (23), 206 (52), 151 (63), 135 (36), 109 (28), 68 (30).

The above mentioned C(6)-ketone (2.0 g; 6.58 mmol) was isomerized into the conjugated ketone **7** by treatment with an 1 M solution of sodium methoxide (5 mL) in methanol (35 mL) at room temperature during 2 h. The methanol was evaporated and an 1 M aquous solution of HCl (200 mL) was added. Extraction with ether followed by usual work up gave the crude product which was purified by flash column chromatography (PE/EA 2:1) to give compound **7**[24] (1.96 g; 6.45 mmol; 98%) as a light yellow oil. $[\alpha]_D$=+43.5 (*c* 3.6); IR (liquid film) ν_{max} 3429, 3088, 2912, 1651 cm^{-1}; ^1H NMR δ 0.77 (s, 3H), 1.05 (s, 3H), 1.08 (s, 3H), 1.25 (s, 3H), 1.12–1.92 (m, 13H), 1.85 (s, 3H), 5.03 (dd, *J*=1.2, 10.7 Hz, 1H), 5.17 (dd, *J*=1.2, 17.3 Hz, 1H), 5.68 (t, *J*=1.4 Hz, 1H), 5.86 (dd, *J*=10.7, 17.3 Hz, 1H); ^{13}C NMR δ 14.6 (q), 18.2 (t), 21.4 (t), 21.5 (q), 22.1 (q), 27.8 (q), 32.3 (s), 33.4 (q), 38.7 (t), 43.2 (t), 43.4 (s), 44.6 (t), 56.6 (d), 63.6 (d), 73.4 (s), 112.3 (t), 128.4 (d), 144.6 (d), 159.0 (s), 200.4 (s); HRMS: M^+, found 304.2394. $C_{20}H_{32}O_2$ requires 304.2402; MS *m/e* (%) 286 [(M^+−18), 17], 219 (19), 218 (34), 135 (100), 109 (28), 95 (21), 73 (89), 43 (31).

3.2. General procedure for the oxidation with 1.5 equiv. of potassium permanganate

To an ice-cooled stirred solution of labdanes **1**–**7** (3.25 mmol) and *N*,*N*,*N*′-triethylbenzenemethanaminium chloride (1.1 g; 4.91 mmol) in dichloromethane (40 mL) was added solid $KMnO_4$ (0.77 g; 4.91 mmol) in small portions in 15 min and then the mixture was allowed to warm up to room temperature and stirring was continued until conversion of the starting material, which took about 14 h. The dark brown reaction mixture was treated with an aqueous saturated Na_2SO_3 solution (75 mL) and with a 3% aqueous solution of oxalic acid (75 mL). Extraction of the now colourless reaction mixture with ethyl acetate was followed by usual work-up and purification was performed by flash column chromatography. Gradient eluation gave first methyl ketones **11**–**13**, **24** and enol ethers **20**–**22** (eluent PE/EA 3:1), followed by triols **8**–**10**, **23** (eluent EA/MeOH 9:1).

3.2.1. (+)-(2ζ,3*S*)-5-((1*S*,4*S*,4a*S*,8a*R*)-4-Hydroxy-5,5,8a-trimethyl-2-methylenedecahydro-1-naphthalenyl)-3-methyl-1,2,3-pentanetriol (8). Compound **8** was isolated as a white crystalline solid in 38% yield. Mp 139–141°C; $[\alpha]_D$=+33.2 (*c* 1.5, EtOH); IR (KBr) ν_{max} 3389, 2939, 1644, 1382, 1271 cm^{-1}; ^1H NMR δ 0.42 (s, 3H), 0.71 (s, 3H), 0.85 (s, 3H), 0.87 (s, 3H), 1.02–1.84 (m, 17H), 2.34 (dd, *J*=4.8, 12.2 Hz, 1H), 3.14–3.84 (m, 4H), 4.33 (br s, 1H), 4.58 (br s, 1H); ^{13}C NMR δ 15.3 (q), 16.9 (t), 18.6 (t), 21.2 (q), 21.5 (q), 33.3 (s), 35.8 (q), 37.3 (t), 38.8 (t), 38.9 (s), 43.3 (t), 48.2 (t), 56.2 (d), 59.6 (d), 62.4 (t), 70.5 (d), 73.7 (s), 76.1 (d), 107.3 (t), 145.4 (s); HRMS: M^+, found 340.2597. $C_{20}H_{36}O_4$ requires 340.2614; HRMS: (M^+−18), found 322.2509. $C_{20}H_{34}O_3$ requires 322.2508; MS *m/e* (%) 340 (M^+, 3), 322 (11), 261 (49), 243 (58), 218 (58), 153 (71), 109 (87), 95 (66), 69 (100), 43 (75); Anal. found C, 70.24; H, 10.71%. $C_{20}H_{36}O_4$ requires C, 70.55; H, 10.66%.

3.2.2. (+)-(1*S*,4*S*,4a*R*,8a*S*)-4a,8,8-Trimethyl-3-methylene-4-((3*S*,4ζ)-3,4,5-trihydroxy-3-methylpentyl)-decahydro-1-naphthalenyl acetate (9). Compound **9** was isolated as an oil in 26% yield. $[\alpha]_D$=+24.6 (*c* 1.9); IR (liquid film) ν_{max} 3378, 2910, 1720, 1647, 1258 cm^{-1}; ^1H NMR δ 0.71 (s, 3H), 0.83 (s, 3H), 0.97 (s, 3H), 1.10 (s, 3H), 1.16–1.84 (m, 16H), 2.00 (s, 3H), 2.63 (dd, *J*=5.1, 12.2 Hz, 1H), 3.43 (t, *J*=4.3 Hz, 1H), 3.64 (d, *J*=2.6 Hz, 2H), 4.62 (s, 1H), 4.88 (s, 1H), 4.97 (dt, *J*=5.8, 11.0 Hz, 1H); ^{13}C NMR δ 16.0 (q), 17.5 (t), 19.0 (t), 22.0 (2×q), 22.1 (q), 33.5 (s), 36.2 (q), 38.3 (t), 39.1 (t), 39.6 (s), 43.5 (t), 44.2 (t), 56.5 (d), 57.5 (d), 63.3 (t), 73.3 (d), 74.6 (s), 75.9 (d), 109.4 (s), 144.3 (s), 170.3 (s); HRMS: (M^+−18), found 364.2609. $C_{22}H_{36}O_4$

requires 364.2614; MS *m/e* (%) 382 (M^+, 2), 364 (3), 322 (26), 243 (83), 189 (44), 188 (43), 153 (54), 123 (34), 109 (30), 105 (29), 95 (29), 81 (31), 43 (100).

3.2.3. (+)-(2ζ,3*R*)-5-((1*S*,4a*S*,8a*S*)-5,5,8a-Trimethyl-2-methylenedecahydro-1-naphthalenyl)-3-methyl-1,2,3-pentanetriol (10). Compound **10** was isolated as a white crystalline solid in 24% yield, as its hydrate. Mp 129–131°C; $[\alpha]_D$=+20.8 (*c* 0.53); IR (KBr) ν_{max} 3418, 2943, 2476, 3082, 1639, 1458, 1387 cm^{-1}; ^1H NMR δ 0.62 (s, 3H), 0.73 (s, 3H), 0.81 (s, 3H), 1.06 (s, 3H), 1.10–1.96 (m, 16H), 2.28 (dd, *J*=4.0, 12.1 Hz, 1H), 3.36–3.66 (m, 5H), 4.46 (br s, 1H), 4.73 (br s, 1H); ^{13}C NMR δ 14.3 (q), 17.1 (t), 19.2 (t), 21.5 (q), 21.7 (q), 24.3 (t), 33.3 (s), 33.4 (q), 36.0 (t), 36.2 (t), 36.9 (t), 39.7 (s), 42.0 (t), 55.4 (d), 57.3 (d), 62.9 (t), 74.3 (s), 75.9 (d), 106.2 (t), 146.6 (s); HRMS: M^+, found 324.2664. $C_{20}H_{36}O_3$ requires 324.2664; MS *m/e* (%) 324 (M^+, 6), 306 (10), 275 (28), 245 (100), 204 (38), 137 (81), 121 (42), 109 (43), 95 (61), 69 (58), 43 (52); Anal. found C, 70.45; H, 11.14%. $C_{20}H_{36}O_3 \cdot H_2O$ requires C, 70.13; H, 11.18%.

3.2.4. (+)-4-((1*S*,4*S*,4a*S*,8a*R*)-4-Hydroxy-5,5,8a-trimethyl-2-methylenedecahydro-1-naphthalenyl)-2-butanone (11). Methyl ketone **11** was isolated as a white crystalline solid in 45% yield. Mp 77–79°C; $[\alpha]_D$=+43.4 (*c* 2.0); IR (liquid film) ν_{max} 3467, 2926, 1713, 1644, 1361 cm^{-1}; ^1H NMR δ 0.69 (s, 3H), 0.99 (s, 3H), 1.15 (s, 3H), 1.07–2.06 (m, 14H), 2.10 (s, 3H), 2.66 (dd, *J*=4.9, 12.1 Hz, 1H), 3.82 (dt, *J*=4.9, 10.6 Hz, 1H), 4.49 (d, *J*=1.2 Hz, 1H), 4.88 (d, *J*=1.2 Hz, 1H); ^{13}C NMR δ 15.9 (q), 17.7 (t), 19.1 (t), 22.3 (q), 30.1 (q), 33.9 (s), 36.6 (q), 39.2 (t), 39.4 (s), 42.8 (t), 43.6 (t), 49.0 (t), 55.4 (d), 60.4 (d), 71.6 (d), 108.2 (t), 145.3 (s), 209.2 (s); HRMS: (M^+−18), found 260.2131. $C_{18}H_{28}O$ requires 260.2140; MS *m/e* (%) 260 [(M^+−18), 76], 202 (53), 153 (52), 109 (55), 95 (38), 93 (72), 43 (100); Anal. found C, 78.12; H, 11.28%. $C_{18}H_{30}O_2$ requires C, 77.65; H, 10.86%.

3.2.5. (+)-(1*S*,4*S*,4a*R*,8a*S*)-4a,8,8-Trimethyl-3-methylene-4-(3-oxobutyl)-decahydro-1-naphthalenyl acetate (12). Methyl ketone **12** was isolated as a colourless oil in 48% yield. $[\alpha]_D$=+56.2 (*c* 1.8); IR (liquid film) ν_{max} 2929, 1733, 1717, 1647, 1243 cm^{-1}; ^1H NMR δ 0.71 (s, 3H), 0.83 (s, 3H), 0.91 (s, 3H), 2.02 (s, 3H), 2.07 (s, 3H), 1.01–2.42 (m, 13H), 2.64 (dd, *J*=5.1, 12.2 Hz, 1H), 4.51 (d, *J*=1.3 Hz, 1H), 4.89 (d, *J*=1.3 Hz, 1H), 4.97 (dt, *J*=5.1, 10.9 Hz, 1H); ^{13}C NMR δ 15.8 (q), 17.6 (t), 18.9 (t), 21.9 (q), 22.4 (q), 30.0 (q), 33.4 (s), 36.1 (q), 38.9 (t), 39.6 (s), 42.6 (t), 43.3 (t), 44.0 (t), 55.2 (d), 57.4 (d), 73.1 (d), 109.2 (t), 144.0 (s), 170.0 (s), 209.0 (s); HRMS: (M^+−60), found 260.2146. $C_{18}H_{28}O$ requires 260.2140; MS *m/e* (%) 260 [(M^+−60), 76], 202 (88), 189 (35), 187 (32), 159 (19), 153 (57), 135 (21), 133 (36), 123 (22), 43 (100).

3.2.6. (+)-(1*S*,4*S*,4a*R*,8a*S*)-4a,8,8-Trimethyl-3-methylene-4-(3-oxobutyl)-decahydro-1-naphthalenyl acetate (12). To a solution of methyl ketone **11** (0.7 g; 2.52 mmol) in CH_2Cl_2 (20 mL) and pyridine (15 mL) was added acetic anhydride (2.17 g; 21.3 mmol) and 4-*N*,*N*-dimethylaminopyridine (25 mg; 0.20 mmol). The reaction mixture was stirred for 1 h, then poured into a 4 M aqueous solution of HCl, and worked up with ethyl acetate. Purification by flash column chromatography on silica gel (eluent PE/EA 15:1) gave acetate **12** (0.73 g; 2.29 mmol; 91%) as a colourless oil. Spectral data of **12** were identical with the above mentioned.

3.2.7. (+)-4-((1*S*,4a*S*,8a*S*)-5,5,8a-Trimethyl-2-methylenedecahydro-1-naphthalenyl)-2-butanone (13). Methyl ketone **13** was isolated as a colourless oil in 48% yield. $[\alpha]_D$=+35.5 (*c* 1.8); IR (liquid film) ν_{max} 3477, 2931, 3078, 1716, 1460, 1366, 1162 cm^{-1}; ^1H NMR δ 0.44 (s, 3H), 0.55 (s, 3H), 0.62 (s, 3H), 1.02–1.79 (m, 15H), 1.85 (s, 3H), 2.29 (dd, *J*=4.2, 12.1 Hz, 1H), 4.19 (d, *J*=0.9 Hz, 1H), 4.57 (d, *J*=0.9 Hz, 1H); ^{13}C NMR δ 14.3 (q), 17.5 (t), 19.3 (t), 21.7 (q), 24.4 (t), 30.1 (q), 33.6 (2×q), 38.3 (t), 39.0 (t), 39.8 (s), 42.1 (t), 42.9 (t), 55.5 (d), 56.2 (d), 106.3 (t), 148.3 (s), 209.6 (s); HRMS: M^+, found 262.2300. $C_{18}H_{30}O$ requires 262.2297; MS *m/e* (%) 262 (M^+, 52), 244 (48), 204 (51), 177 (40), 137 (100), 123 (36), 107 (40), 95 (55), 81 (51), 43 (56).

3.2.8. (+)-(2ζ,3*S*)-5-((1*R*,2*R*,4a*S*,8a*S*)-2-Hydroxy-2,5,5,8a-tetramethyldecahydro-1-naphthalenyl)-3-methyl-1,2,3-pentanetriol (16). Compound **16** was isolated as a colourless oil in 25% yield. $[\alpha]_D$=+0.9 (*c* 1.5); IR (KBr) ν_{max} 3405, 2927, 2860, 1464, 1387, 1085 cm^{-1}; ^1H NMR δ 0.73–1.20 (5×s, 5×3H), 1.26–1.98 (m, 18H), 3.31–3.77 (m, 5H); ^{13}C NMR δ 15.5 (q), 18.1 (t), 18.4 (t), 20.4 (t), 21.2 (q), 21.4 (q), 23.9 (q), 33.2 (s), 33.9 (q), 39.2 (s), 39.5 (t), 41.3 (t), 42.0 (t), 43.6 (t), 56.1 (d), 61.8 (d), 63.0 (t), 74.4 (s), 78.1 (d), 78.7 (s); HRMS: M^+, found 342.2764. $C_{20}H_{38}O_4$ requires 342.2770; MS *m/e* (%) 342 (M^+, 2), 324 (9), 306 (13), 245 (100), 177 (39), 137 (37), 109 (46), 95 (49), 81 (41), 69 (50), 43 (64).

3.2.9. (+)-4-((1*R*,2*R*,4a*S*,8a*S*)-2-Hydroxy-2,5,5,8a-tetramethyldecahydro-1-naphthalenyl)-2-butanone (19). Methyl ketone **19** was isolated as a colourless oil in 6% yield. After its isolation this methyl ketone quickly cyclized to sclareol oxide (**22**). $[\alpha]_D$=+7.3 (*c* 1.3) (lit.[42]: +6.7, *c* 1.0); IR (liquid film) ν_{max} 3439, 2924, 2866, 1731, 1683, 1459, 1376, 1248, 1048 cm^{-1}; ^1H NMR δ 0.75 (s, 3H), 0.78 (s, 3H), 0.83 (s, 3H), 1.12 (s, 3H), 1.50–2.05 (m, 15H), 2.10 (s, 3H), 2.48–2.60 (m, 1H), 2.60–2.70 (m, 1H); MS *m/e* (%) 280 (M^+, 1), 262 (100), 191 (81), 177 (39), 123 (46), 109 (97), 95 (64), 43 (78).

3.2.10. (4a*R*,6*S*,6a*S*,10a*S*,10b*R*)-3,4a,7,7,10a-Pentamethyl-4a,5,6,6a,7,8,9,10,10a,10b-decahydro-1*H*-benzo[*f*]chromen-6-ol (20). Compound **20** was isolated as a colourless oil in 47% yield. $[\alpha]_D$=+24.9 (*c* 0.4); ^1H NMR δ 0.82 (s, 3H), 1.00 (s, 3H), 1.13 (s, 3H), 1.15 (s, 3H), 1.75 (s, 3H), 1.10–1.94 (m, 12H), 2.23 (dd, *J*=3.9, 11.8 Hz, 1H), 3.89 (dt, *J*=3.9, 11.2 Hz, 1H), 4.42 (br d, *J*=2.9 Hz, 1H); ^{13}C NMR δ 16.2 (q), 18.3 (t), 18.6 (t), 20.3 (q), 21.2 (q), 22.0 (q), 33.6 (s), 36.6 (q), 37.4 (s), 39.3 (t), 43.6 (t), 52.0 (d), 52.1 (t), 61.4 (d), 68.9 (d), 75.5 (s), 94.7 (d), 147.8 (s); HRMS: M^+, found 278.2241. $C_{18}H_{30}O_2$ requires 278.2246; MS *m/e* (%) 278 (M^+, 99), 245 (29), 217 (100), 215 (30), 191 (53), 189 (52), 175 (44), 119 (30), 109 (39).

3.2.11. (4a*R*,6*S*,6a*S*,10a*S*,10b*R*)-3,4a,7,7,10a-Pentamethyl-4a,5,6,6a,7,8,9,10,10a,10b-decahydro-1*H*-benzo[*f*]chromen-6-yl acetate (21). Compound **21** was isolated as a colourless oil in 48% yield. ^1H NMR δ 0.87 (s, 3H), 0.89 (s, 3H), 1.02 (s, 3H), 1.21 (s, 3H), 1.23–1.89 (m, 14H), 2.04

(s, 3H), 2.17 (dd, J=4.1, 11.7 Hz, 1H), 4.41–4.44 (m, 1H), 5.12 (dt, J=4.1, 11.3 Hz, 1H); ^{13}C NMR δ 16.1 (q), 18.2 (t), 18.5 (t), 20.2 (q), 21.0 (q), 21.9 (q), 22.1 (q), 33.2 (s), 36.2 (q), 37.5 (s), 39.1 (t), 43.3 (t), 47.5 (t), 51.9 (d), 58.4 (d), 70.5 (d), 75.1 (s), 94.6 (d), 147.8 (s), 170.2 (s); HRMS: M^+, found 320.2350. $C_{20}H_{32}O_3$ requires 320.2351; MS *m/e* (%) 320 (M^+, 5), 260 (37), 190 (34), 189 (90), 119 (100), 109 (36), 69 (33), 43 (95).

3.2.12. (+)-(4a*R*,6a*S*,10a*S*,10b*R*)-3,4a,7,7,10a-Pentamethyl-4a,5,6,6a,7,8,9,10,10a,10b-decahydro-1*H*-benzo[*f*]chromene, (sclareol oxide (22)). Compound **22** was isolated as a light yellow oil in 51% yield. $[\alpha]_D$=+4.9 (*c* 1.3) (lit.[42]: $[\alpha]_D$=+5.7, *c* 1.6); IR (liquid film) ν_{max} 3055, 2950, 2900, 2890, 1687, 1470, 1390, 1342, 1000 cm^{-1}; ^{1}H NMR δ 0.74 (s, 6H), 0.81 (s, 3H), 1.25 (s, 3H), 1.61 (s, 3H), 1.76–1.83 (m, 13H), 1.87 (dt, J=.3, 14.6 Hz, 1H), 4.30 (br s, 1H); ^{13}C NMR δ 19.3 (q), 18.2 (q), 18.6 (t), 19.8 (t), 20.7 (q), 21.0 (q), 26.6 (q), 28.6 (q), 33.1 (s), 36.7 (s), 39.3 (t), 41.1 (t), 41.9 (t), 52.4 (d), 55.2 (d), 76.2 (s), 94.6 (d), 147.8 (s); HRMS: M^+, found 262.2294. $C_{18}H_{30}O$ requires 262.2297; MS *m/e* (%) 262 (M^+, 100), 191 (81), 177 (39), 123 (46), 109 (97), 95 (64), 81 (72), 43 (78).

3.2.13. (+)-(4*S*,4a*R*,8a*S*)-3,4a,8,8-Tetramethyl-4-((3*S*)-3,4,5-trihydroxy-3-methylpentyl)-4a,5,6,7,8,8a-hexahydro-1(4*H*)-naphthalenone (23). Compound **23** was isolated as a white crystalline solid in 56% yield. Mp 108–110°C; $[\alpha]_D$=+21.0 (*c* 1.1); IR (KBr) ν_{max} 3422, 2928, 1669, 1384, 1293, 1234, 1087 cm^{-1}; ^{1}H NMR δ 0.77 (s, 3H), 1.04 (s, 3H), 1.06 (s, 3H), 1.12 (s, 3H), 1.90 (s, 3H), 1.12–1.94 (m, 15H), 3.48 (t, J=4.2 Hz, 1H), 3.76 (d, J=4.2 Hz, 2H), 5.72 (br s, 1H); ^{13}C NMR δ 14.6 (q), 18.0 (t), 21.0 (t), 21.4 (q), 21.9 (q), 22.2 (q), 33.3 (q), 38.6 (t), 41.8 (t), 43.0 (t), 43.4 (s), 43.5 (s), 56.7 (d), 63.3 (t), 63.5 (d), 74.5 (s), 74.8 (d), 128.3 (d), 159.1 (s), 200.6 (s); HRMS: M^+, found 338.2449. $C_{20}H_{34}O_4$ requires 338.2457; MS 338 (M^+, 10), 320 (13), 277 (17), 219 (49), 218 (73), 203 (12), 148 (14), 135 (100), 109 (18), 73 (17), 69 (18), 43 (22); Anal. found C, 70.82; H, 10.12%. $C_{20}H_{34}O_4$ requires C, 70.97; H, 10.13%.

3.2.14. (+)-(4*S*,4a*R*,8a*S*)-3,4a,8,8-Tetramethyl-4-(3-oxobutyl)-4a,5,6,7,8,8a-hexahydro-1(4*H*)-naphthalenon (24). Methyl ketone **24** was isolated as a colourless oil in 8% yield. $[\alpha]_D$=+34.0 (*c* 1.4); IR (liquid film) ν_{max} 2928, 1716, 1669, 1454, 1357, 1176 cm^{-1}; ^{1}H NMR δ 0.79 (s, 3H), 1.06 (s, 3H), 1.09 (s, 3H), 1.84 (s, 3H), 1.14–2.06 (m, 10H), 2.11 (s, 3H), 2.47–2.70 (m, 2H), 5.70 (dd, J=1.3, 2.7 Hz, 1H); ^{13}C NMR δ 14.6 (q), 18.1 (t), 20.5 (t), 21.4 (q), 22.1 (q), 30.0 (q), 32.2 (s), 33.4 (q), 38.9 (t), 43.0 (t), 43.4 (s), 45.4 (t), 55.5 (d), 63.5 (d), 128.8 (d), 158.0 (s), 200.3 (s), 207.9 (s); HRMS: M^+, found 276.2082. $C_{18}H_{28}O_2$ requires 276.2089; MS *m/e* (%) 276 (M^+, 2), 219 (6), 135 (19), 109 (13), 95 (6), 73 (100), 69 (2), 43 (30), 41.

3.2.15. (+)-(4*S*,4a*R*,8a*S*)-3,4a,8,8-Tetramethyl-4-(3-oxobutyl)-4a,5,6,7,8,8a-hexahydro-1(4*H*)-naphthalenon (24). To a solution of **7** (1.0 g; 3.29 mmol) and benzyltriethylammonium chloride (2.21 g; 9.87 mmol) in dichloromethane (40 mL) was added solid $KMnO_4$ (1.55 g; 9.87 mmol) at once at room temperature. The mixture was stirred until completion of the reaction. The dark brown reaction mixture was treated with an aqueous saturated Na_2SO_3 solution and a 3% aqueous solution of oxalic acid. Extraction of the colourless reaction mixture with ethyl acetate was followed by usual work-up. Purification by flash column chromatography (eluent PE/EA 3:1) gave methyl ketone **24** (0.68 g; 2.24 mmol; 68%) as a colourless oil. The analytical data were as mentioned before.

3.3. (+)-4-((1*S*,4*S*,4a*S*,8a*R*)-4-((*tert*-Butyl(dimethyl)-silyl)oxy)-5,5,8a-trimethyl-2-methylenedecahydro-1-naphthalenyl)-2-butanone (25)

A mixture of methyl ketone **11** (0.30 g; 1.08 mmol), *tert*-butyldimethylsilyl chloride (1.63 g; 10.79 mmol) and imidazole (1.47 g; 21.58 mmol) in DMF (25 mL) was stirred at 60°C. After heating overnight the mixture was cooled to room temperature, diluted with ether, washed with H_2O and worked up as usual. The crude yellow oil was purified by flash column chromatography (eluent PE/EA 10:1) to give silyl ether **25** as an oil (0.32 g; 0.91 mmol; 84%). $[\alpha]_D$=+40.7 (*c* 0.7); IR (liquid film) ν_{max} 2928, 2856, 1720, 1471, 1463, 1361, 1233 cm^{-1}; ^{1}H NMR δ 0.11 (s, 3H), 0.13 (s, 3H), 0.71 (s, 3H), 0.90 (s, 9H), 0.96 (s, 3H), 1.13 (s, 3H), 2.12 (s, 3H), 1.16–2.42 (m, 12H), 2.57 (m, 2H), 3.85 (dt, J=4.6, 10.4 Hz, 1H), 4.48 (br s, 1H), 4.85 (br s, 1H); ^{13}C NMR δ −3.7 (q), −3.5 (q), 16.0 (q), 17.7 (t), 18.1 (s), 19.0 (t), 22.3 (q), 26.1 (3×q), 30.1 (q), 33.7 (s), 36.5 (q), 39.3 (s), 39.6 (t), 42.9 (t), 44.1 (t), 49.6 (t), 55.5 (d), 60.0 (d), 72.6 (d), 107.8 (t), 145.9 (s), 209.4 (s); HRMS: (M^+−15), found 377.2878. $C_{23}H_{41}O_2Si$ requires 377.2876; MS *m/e* (%) 392 (M^+, 2), 377 (3), 335 (49), 267 (36), 243 (100), 211 (63), 119 (26), 43 (21).

3.4. Baeyer–Villiger oxidation with *m*-chloroperbenzoic acid of 11

A mixture of methyl ketone **11** (0.20 g; 0.72 mmol) and *m*-CPBA (0.35 g; 1.51 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 13 days. Ether was added and the mixture was washed with a 2% aqueous $Na_2S_2O_3$ solution, saturated aqueous sodium bicarbonate, brine, dried and evaporated. Flash column chromatography (eluent PE/EA 5:1) gave epoxy acetate **26** (0.07 g; 0.22 mmol; 31%), acetal **28** (0.085 g; 0.29 mmol; 40%), and epoxide **30** (0.025 g; 0.09 mmol; 12%), respectively.

3.4.1. (+)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-2-(4-Hydroxy-3,4,4a,5,6,7,8,8a-octahydro-5,5,8a-trimethyl-spiro[naphtalene-2(1*H*),2′-oxiran]-yl-ethyl acetate (26). Colourless oil; $[\alpha]_D$=+16.7 (*c* 1.1); IR (liquid film) ν_{max} 3480, 3002, 2930, 2869, 1738, 1714, 1248, 1034 cm^{-1}; ^{1}H NMR δ 0.83 (s, 3H), 0.99 (s, 3H), 1.19 (s, 3H), 1.05–1.98 (m, 13H), 2.05 (s, 3H), 2.59 (d, J=4.1 Hz, 1H), 2.76 (dd, J=1.9, 4.1 Hz, 1H), 4.03 (dt, J=3.8, 10.4 Hz, 1H), 3.95–4.14 (m, 2H); ^{13}C NMR δ 15.8 (q), 18.2 (t), 21.0 (q), 21.5 (t), 22.2 (q), 33.7 (s), 36.5 (q), 39.6 (s), 43.6 (t), 46.7 (t), 49.6 (d), 50.8 (t), 57.0 (s), 60.1 (d), 65.2 (t), 69.7 (d), 171.6 (s); HRMS: M^+, found 310.2139. $C_{18}H_{30}O_4$ requires 310.2144; MS *m/e* (%) 310 (M^+, 1), 250 (27), 153 (39), 126 (48), 109 (100), 98 (48), 69 (70), 43 (82).

3.4.2. (+)-(3*S*,4*S*,9*S*,10*R*)-5,5,9,13-Tetramethyl-14,16-dioxatetracyclo[11.2.1.0^{1,10}.0^{4,9}]hexade-can-3-ol (28). Crystalline

solid; mp 126–128°C; $[\alpha]_D$=+17.1 (*c* 1.0); IR (KBr) ν_{max} 3457, 2985, 2923, 2849, 1460, 1385, 1030 cm^{-1}; ^1H NMR δ 1.09 (s, 3H), 1.14 (s, 3H), 1.18 (s, 3H), 1.45 (s, 3H), 0.91–1.85 (m, 14H), 2.10 (dd, *J*=4.3, 13.4 Hz, 1H), 3.38 (d, *J*=6.8 Hz, 1H), 3.81 (d, *J*=6.8 Hz, 1H), 4.19 (dt, *J*=4.3, 11.0 Hz, 1H); ^{13}C NMR δ 16.9 (t), 17.8 (q), 18.3 (t), 22.5 (q), 24.9 (q), 33.6 (s), 33.6 (t), 37.2 (q), 40.3 (t), 40.4 (s), 43.9 (t), 45.6 (t), 49.6 (d), 59.8 (d), 68.2 (d), 75.8 (t), 82.4 (s), 108.6 (s); HRMS: M^+, found 294.2198. $C_{18}H_{30}O_3$ requires 294.2195; MS *m/e* (%) 294 (M^+, 11), 234 (71), 206 (100), 191 (33), 188 (44), 173 (30), 109 (35), 95 (28), 69 (36), 43 (45); Anal. found C, 73.19; H, 10.47%. $C_{18}H_{30}O_3$ requires C, 73.43; H, 10.27%.

3.4.3. (+)-(1*S*,4*S*,4a*S*,8a*R*)-4-(4-Hydroxy-octahydro-5,5,8a-trimethyl-spiro[naphtalene-2(1*H*),2′-oxiran]-yl)-2-butanone (30). Colourless oil; $[\alpha]_D$=+19.1 (*c* 0.4); IR (liquid film) ν_{max} 3479, 2928, 2870, 1714, 1462, 1386, 1362 cm^{-1}; ^1H NMR δ 0.81 (s, 3H), 0.97 (s, 3H), 1.15 (s, 3H), 1.04–2.02 (m, 15H), 2.07 (s, 3H), 2.48–2.55 (m, 1H), 2.80 (dd, *J*=1.9, 4.3 Hz, 1H), 3.98 (dt, *J*=4.5, 10.9 Hz, 1H); ^{13}C NMR δ 15.8 (q), 16.0 (t), 18.3 (t), 22.2 (q), 29.9 (q), 33.7 (s), 36.5 (q), 39.1 (t), 40.1 (s), 43.5 (t), 47.0 (t), 51.0 (t), 52.2 (d), 57.8 (s), 60.0 (d), 69.6 (d), 75.7 (t), 209.2 (s); HRMS: M^+, found 294.2200. $C_{18}H_{30}O_3$ requires 294.2195; MS *m/e* (%) 294 (M^+, 6), 234 (44), 206 (61), 153 (32), 109 (81), 95 (48), 81 (45), 69 (67), 43 (100).

3.5. Baeyer–Villiger oxidation with *m*-chloroperbenzoic acid of 25

A mixture of silyl ether **25** (0.10 g; 0.25 mmol) and *m*-CPBA (0.18 g; 0.71 mmol) in CH_2Cl_2 (8 mL) was stirred at room temperature for 48 h. Ether was added and the mixture was washed with a 2% aqueous solution of sodium thiosulfate, saturated aqueous sodium bicarbonate, brine, dried and evaporated. Flash column chromatography (eluent PE/EA 15:1) of the crude product gave acetal **29** (0.023 g; 0.056 mmol; 20%), epoxy acetate **27** (0.020 g; 0.047 mmol; 17%), and epoxide **31** (0.050 g; 0.12 mmol; 48%), respectively. During the identification procedure epoxide **31** is converted into acetal **29**.

3.5.1. (+)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-2-(4-[(1,1-Dimethylethyl)-dimethylsilyl]oxy-3,4,4a,5,6,7,8,8a-octahydro-5,5,8a-trimethyl-spiro[naphtalene-2(1*H*),2′-oxiran]-yl-ethyl acetate (27). Oil; $[\alpha]_D$=+6.2 (*c* 1.1); IR (liquid film) ν_{max} 2927, 2854, 1724, 1224, 1208 cm^{-1}; ^1H NMR δ −0.01 (s, 3H), 0.00 (s, 3H), 0.73 (s, 3H), 0.78 (s, 9H), 0.89 (s, 3H), 1.08 (s, 3H), 1.07–1.72 (m, 12H), 1.95 (s, 3H), 2.44 (d, *J*=4.1 Hz, 1H), 2.66 (dd, *J*=2.0, 4.1 Hz, 1H), 3.88–4.02 (m, 3H); ^{13}C NMR δ −4.0 (q), −3.5 (q), 16.0 (q), 18.1 (s), 18.2 (t), 21.1 (q), 21.5 (t), 22.2 (q), 26.0 (3×q), 33.6 (s), 36.4 (q), 39.5 (t), 39.6 (s), 44.0 (t), 47.2 (t), 49.5 (d), 50.8 (t), 57.1 (s), 59.7 (d), 65.3 (t), 70.5 (d), 171.1 (s); HRMS: (M^+−15), found 409.2772. $C_{23}H_{41}O_4Si$ requires 409.2774; MS *m/e* (%) 409 [(M^+−15), 1], 367 (21), 233 (71), 215 (78), 183 (57), 109 (44), 105 (43), 69 (49), 43 (41), 32 (100).

3.5.2. (+)-(1*R*,3*S*,4*S*,9*S*,10*R*)-*tert*-Butyl(dimethyl)silyl-5,5,9,13-tetramethyl-14,16-dioxatetracyclo[11.2.1.0^{1,10}.0^{4,9}]-hexadec-3-yl ether (29). Crystals; mp 54–56°C; $[\alpha]_D$=+29.6 (*c* 0.7); IR (KBr) ν_{max} 3442, 2929, 1385, 1253, 1061 cm^{-1}; ^1H NMR δ −0.02 (s, 3H), 0.00 (s, 3H), 0.76 (s, 3H), 0.77 (s, 9H), 0.90 (s, 3H), 1.02 (s, 3H), 1.28 (s, 3H), 1.87 (dd, *J*=4.2, 13.3 Hz, 1H), 0.95–1.80 (m, 13H), 3.23 (d, *J*=6.7 Hz, 1H), 3.62 (d, *J*=6.7 Hz, 1H), 4.06 (dt, *J*=4.2, 10.6 Hz, 1H); ^{13}C NMR δ −3.7 (q), −3.6 (q), 17.0 (t), 17.9 (q), 18.1 (s), 18.2 (t), 22.4 (q), 25.0 (q), 26.2 (3×q), 33.4 (s), 33.6 (t), 37.0 (q), 40.1 (s), 40.8 (t), 44.4 (t), 46.0 (t), 49.7 (d), 59.8 (d), 69.1 (d), 76.0 (t), 82.3 (s), 108.5 (s); HRMS: M^+, found 408.3050. $C_{24}H_{44}O_2Si$ requires 408.3060; MS *m/e* (%) 408 (M^+, 2), 352 (27), 351 (100), 275 (14), 119 (9), 117 (11), 75 (26), 43 (10); Anal. found C, 70.68; H, 11.14%. $C_{24}H_{44}O_3Si$ requires C, 70.54; H, 10.85%.

3.5.3. (+)-(1*S*,4*S*,4a*S*,8a*R*)-4-(4-[(1,1-Dimethylethyl)dimethylsilyl]oxy-octahydro-5,5,8a-trimethyl-spiro[naphtalene-2(1*H*),2′-oxiran]-yl)-2-butanone (31). ^1H NMR δ 0.05 (s, 3H), 0.07 (s, 3H), 0.83 (s, 3H), 0.87 (s, 9H), 0.97 (s, 3H), 1.12 (s, 3H), 1.08–1.98 (m, 12H), 1.58 (dd, *J*=3.8, 11.2 Hz, 1H), 2.09 (s, 3H), 2.32–2.65 (m, 2H), 2.82 (dd, *J*=2.1, 4.2 Hz, 1H), 4.03 (dt, *J*=4.5, 10.7 Hz, 1H).

3.6. Baeyer–Villiger oxidation with *m*-chloroperbenzoic acid of 12

A mixture of acetate **12** (0.20 g; 0.62 mmol) and *m*-CPBA (0.38 g; 1.56 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 10 days. Ether was added and the mixture was washed with a 2% aqueous solution of $Na_2S_2O_3$, saturated aqueous sodium bicarbonate, and worked up as usual. Flash column chromatography (eluent PE/EA 5:1) afforded epoxy diacetate **34** (0.187 g; 0.53 mmol; 84%) as white crystals. Further elution gave epoxy methyl ketone **33** (0.023 g; 0.069 mmol; 11%) as an oil.

3.6.1. (+)-(1*S*,4*S*,4a*S*,8a*R*)-4-(4-Acetoxy-octahydro-5,5,8a-trimethyl-spiro[naphtalene-2(1*H*),2′-oxiran]-yl)-2-butanone (33). IR (KBr) ν_{max} 2929, 2869, 1731, 1714, 1366, 1244, 1027 cm^{-1}; ^1H NMR δ 0.85 (s, 3H), 0.88 (s, 3H), 0.99 (s, 3H), 1.03–1.99 (m, 12H), 2.04 (s, 3H), 2.09 (s, 3H), 2.27–2.85 (m, 3H), 2.82 (dd, *J*=1.9, 4.2 Hz, 1H), 5.19 (dt, *J*=5.0, 11.2 Hz, 1H); ^{13}C NMR δ 15.8 (q), 16.1 (t), 18.3 (t), 21.8 (q), 22.3 (q), 29.7 (s), 29.9 (q), 36.1 (q), 39.0 (t), 40.2 (s), 42.5 (t), 43.3 (t), 44.6 (t), 50.9 (t), 52.1 (d), 57.2 (d), 57.4 (s), 71.2 (d), 170.0 (s), 208.9 (s); HRMS: (M^+−60), found 276.2085. $C_{18}H_{28}O_2$ requires 276.2089; MS *m/e* (%) 336 (M^+, 2), 292 (10), 276 (26), 203 (38), 189 (30), 188 (29), 187 (100), 109 (38), 95 (29), 69 (40), 43 (87).

3.6.2. (+)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-2-(4-Acetoxy-3,4,4a,5,6,7,8,8a-octahydro-5,5,8a-trimethyl-spiro[naphtalene-2(1*H*),2′-oxiran]-1β-yl-ethyl acetate (34). Mp 86–88°C; $[\alpha]_D$=+8.4 (*c* 1.2); IR (KBr) ν_{max} 2928, 1721, 1735, 1245 cm^{-1}; ^1H NMR δ 0.89 (s, 3H), 0.91 (s, 3H), 1.06 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 1.11–2.03 (m, 12H), 2.67 (d, *J*=4.1 Hz, 1H), 2.77 (dd, *J*=2.0, 4.1 Hz, 1H), 4.03 (dt, *J*=1.5, 7.0 Hz, 2H), 5.21 (dt, *J*=5.0, 11.2 Hz, 1H); ^{13}C NMR δ 15.8 (q), 18.2 (t), 21.0 (q), 21.5 (t), 21.8 (q), 22.3 (q), 33.4 (s), 36.1 (q), 39.0 (t), 39.8 (s), 42.1 (t), 43.3 (t), 49.6 (d), 50.7 (t), 56.6 (s), 57.2 (d), 65.1 (t), 71.1 (d), 170.0 (s), 171.0 (s); HRMS: (M^+−60), found 292.2036. $C_{18}H_{28}O_3$ requires 292.2038; MS *m/e* (%) 292 [(M^+−60), 35], 232 (96), 217 (65), 187 (24), 153 (24), 109 (33), 43 (100); Anal.

found C, 68.08; H, 9.27%. $C_{20}H_{32}O_5$ requires C, 68.15; H, 9.15%.

3.7. (+)-(1*S*,4*S*,4a*S*,8a*R*)-4-(4-[(1,1-Dimethylethyl)-dimethylsilyl]oxy-octahydro-5,5,8a-trimethyl-spiro-[naphtalene-2(1*H*),2′-oxiran]-yl)-2-butanone (31)

Silyl ether **25** (0.10 g; 0.28 mmol) and MMPP (0.44 g; 0.71 mmol) were dissolved in CH_2Cl_2 (8 mL) and stirred at room temperature for 3 days. Ether was added and the mixture was treated with an aqueous 1 M solution of hydrochloric acid. The aqueous mixture was extracted with ethyl acetate. The combined organic layers were washed with a saturated aqueous sodium bicarbonate solution and worked up as usual. Flash column chromatography (eluent PE/EA 6:1) gave epoxide **31** (0.07 g; 0.17 mmol; 60%) as a colourless oil. $[\alpha]_D$=+17.3 (*c* 0.6); IR (liquid film) ν_{max} 2931, 2868, 1721, 1209 cm^{-1}; ^1H NMR δ 0.05 (s, 3H), 0.07 (s, 3H), 0.83 (s, 3H), 0.87 (s, 9H), 0.97 (s, 3H), 1.12 (s, 3H), 1.08–1.98 (m, 12H), 1.58 (dd, *J*=3.8, 11.2 Hz, 1H), 2.09 (s, 3H), 2.32–2.65 (m, 2H), 2.82 (dd, *J*=2.1, 4.2 Hz, 1H), 4.03 (dt, *J*=4.5, 10.7 Hz, 1H); ^{13}C NMR δ −4.0 (q), −3.5 (q), 16.0 (q), 16.1 (t), 18.1 (s), 18.2 (t), 22.2 (q), 26.0 (3×q), 26.2 (q), 33.6 (s), 36.5 (q), 39.6 (t), 39.8 (s), 44.0 (t), 44.9 (t), 47.6 (t), 51.0 (t), 52.2 (d), 59.8 (d), 70.5 (d), 82.3 (s), 209.1 (s); MS *m/e* (%) 408 (M^+, 2), 367 (2), 233 (44), 215 (100), 159 (32), 145 (34), 117 (38), 105 (33), 75 (64), 73 (44), 69 (39), 43 (36).

3.7.1. (+)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-4-((*tert*-Butyl(dimethyl)-silyl)oxy)-1-(2-hydroxyethyl)-2,5,5,8a-tetramethyldeca-hydro-2-naphthalenol (32).

Epoxy acetate **27** (0.016 g; 0.038 mmol) was dissolved in freshly distilled THF (5 mL), cooled to 0°C and $LiAlH_4$ (0.01 g; 0.15 mmol) was added. After stirring for 3 h at room temperature, the mixture was carefully treated with ethyl acetate and diluted with 4 M HCl. The aqueous mixture was extracted with ethyl acetate, the combined organic layers were washed with brine and worked up as usual. Purification by flash column chromatography (eluent PE/EA 1:1) on silica gel gave compound **32** (0.01 g; 0.023 mmol; 62%) as a sticky colourless oil. $[\alpha]_D$=+33.6 (*c* 0.05); IR (liquid film) ν_{max} 3344, 2929, 2858, 1373, 1027 cm^{-1}; ^1H NMR δ 0.12 (s, 3H), 0.14 (s, 3H), 0.85 (s, 3H), 0.89 (s, 9H), 0.94 (s, 3H), 1.14 (s, 3H), 1.23 (s, 3H), 1.10–1.98 (m, 11H), 2.13 (dd, *J*=3.6, 12.2 Hz, 1H), 2.46 (br s, 2H), 3.47–3.52 (m, 1H), 3.78–3.86 (m, 1H), 3.91 (dt, *J*=3.4, 10.5 Hz, 1H); ^{13}C NMR δ −3.9 (q), −3.5 (q), 16.6 (q), 18.1 (t), 22.0 (q), 25.7 (q), 26.1 (3×q), 27.7 (t), 29.7 (s), 33.6 (s), 36.3 (q), 39.2 (s), 39.8 (t), 43.9 (t), 54.7 (t), 58.4 (d), 60.9 (d), 64.0 (t), 69.7 (d), 72.8 (s); HRMS: (M^+−15−18), found 351.2722. $C_{18}H_{28}O_3$ requires 351.2719; MS *m/e* (%) 351 [(M^+−15−18), 4], 309 (26), 237 (66), 217 (39), 191 (100), 119 (39), 109 (47), 95 (44), 75 (79), 73 (39), 69 (59), 43 (47).

3.7.2. (+)-(1*S*,3*R*,4*R*,4a*S*,8a*S*)-4-(2-Hydroxyethyl)-3,4a, 8,8-tetramethyldecahydro-1,3-naphthalenediol (37).

Epoxy acetate **34** (0.24 g; 0.68 mmol) was dissolved in freshly distilled THF (8 mL), cooled to 0°C and $LiAlH_4$ (110 mg; 2.89 mmol) was added in small portions. After stirring overnight, the mixture was carefully treated with ethyl acetate, and then diluted with a 4 M aqueous solution of hydrochloric acid. The aqueous mixture was extracted with ethyl acetate. The combined organic layers were washed with brine and worked up as usual. The crude oil was purified by flash column chromatography on silica gel (eluent PE/EA 1:1) to give diol **36** (0.155 g; 0.58 mmol; 85%) and triol **37** (0.018 g; 0.068 mmol; 10%) both as white crystalline materials.

3.7.3. (+)-(3a*S*,5*S*,5a*S*,9a*S*,9b*R*)-3a-(Hydroxymethyl)-6, 6,9a-trimethyldodecahydronaphtho[2,1-*b*]furan-5-ol (36).

Mp 133–135°C; $[\alpha]_D$=+11.0 (*c* 0.5); IR (KBr) ν_{max} 3395, 2918, 1472, 1344, 1212, 1015 cm^{-1}; ^1H NMR (400 MHz) δ 0.88 (s, 3H), 0.98 (s, 3H), 1.00 (s, 3H), 1.14–2.03 (m, 10H), 2.17 (dd, *J*=5.6, 15.2 Hz, 1H), 2.87 (br s, 3H), 3.42 (dd, *J*=11.0, 17.8 Hz, 2H), 3.78–3.90 (m, 2H), 4.11 (dt, *J*=1.9, 5.8 Hz, 1H); ^{13}C NMR δ 17.0 (q), 18.3 (t), 22.5 (q), 26.8 (t), 33.7 (s), 33.9 (q), 36.4 (s), 40.1 (t), 42.0 (t), 42.3 (t), 53.8 (d), 59.2 (d), 66.4 (t), 66.4 (d), 68.2 (t), 83.7 (s); HRMS: (M^+−31), found 237.1854. $C_{15}H_{25}O_2$ requires 237.1855; MS *m/e* (%) 238 [(M^+−30), 16], 237 (100), 219 (12), 113 (16), 85 (16), 69 (24), 57 (12), 55 (13), 43 (14), 32 (12); Anal. found C, 72.28; H, 10.81%. $C_{16}H_{28}O_3$ requires C, 71.60; H, 10.52%.

37; Mp 156–158°C; $[\alpha]_D$=+31.4 (*c* 0.8, EtOH); IR (KBr) ν_{max} 3462, 3287, 2925, 2872, 1463, 1378, 1247, 1051 cm^{-1}; ^1H NMR (DMSO-d_6) δ 0.73 (s, 3H), 0.87 (s, 3H), 1.02 (s, 3H), 1.10 (s, 3H), 1.05–1.56 (m, 10H), 1.90 (dd, *J*=3.4, 11.9 Hz, 1H), 2.48 (d, *J*=1.7 Hz, 1H), 3.33 (t, *J*=7.7 Hz, 2H), 3.48–3.55 (m, 1H), 4.09 (br s/m, 3H); ^{13}C NMR ($CDCl_3$/CD_3OD) δ 20.3 (q), 22.0 (t), 25.7 (q), 29.0 (q), 31.6 (t), 37.5 (s), 40.1 (q), 43.1 (s), 43.4 (t), 47.5 (t), 57.7 (t), 62.2 (d), 64.7 (d), 67.4 (t), 72.3 (d), 76.2 (s); HRMS: (M^+−15), found 255.2071. $C_{15}H_{27}O_3$ requires 255.1960; HRMS: (M^+−15−18), found 237.1852. $C_{15}H_{25}O_2$ requires 237.1855; MS *m/e* (%) 270 (M^+, 2), 255 (1), 151 (6), 109 (7), 95 (6), 87 (100), 69 (9), 43 (11); Anal. found C, 71.38; H, 11.35%. $C_{16}H_{30}O_3$ requires C, 71.07; H, 11.18%.

3.7.4. (+)-(1*S*,3*R*,4*R*,4a*S*,8a*S*)-4-(2-Hydroxyethyl)-3,4a, 8,8-tetramethyldecahydro-1,3-naphthalenediol (37).

Aldehyde **43** was treated with $LiAlH_4$ as described above. The triol **37** was obtained in 74% yield as white crystals. For analytical data see foregoing experimental procedure.

An unpurified mixture of aldehyde **44** and acid **47** was reduced as described above. Purification by flash column chromatography (eluent EA/MeOH 95:5) gave the same pure triol **37** as white crystals as obtained before.

Aldehyde **44** was treated with $LiAlH_4$ as above mentioned. The triol **37** was obtained in 87% yield as white crystals. The analytical data were as mentioned before.

Triacetate **52** was dissolved in freshly distilled THF, cooled to 0°C and treated with $LiAlH_4$. Work up as usual and after purification crystalline triol **37** was obtained in 85% yield. The analytical data were as mentioned before.

Triacetate **52** was dissolved in MeOH and treated with an 1 M solution of sodium methoxide in methanol. Usual work up, followed by purification by flash column

chromatography gave triol **37** in 85% yield as white crystals, identical with the product obtained before.

3.7.5. (+)-(1*S*,3*R*,4*R*,4a*S*,8a*S*)-4-(2-Hydroxyethyl)-3,4a,8,8-tetramethyldecahydro-1,3-naphthalenediol (37). A mixture of $CaCO_3$ (0.25 g; 2.50 mmol), PPh_3 (0.65 g; 0.25 mmol), a catalytic amount of $Pd(OAc)_2$ (5 mg) and triacetate **48** (1.0 g; 2.20 mmol) in dioxane (25 mL) was refluxed for 90 min. The mixture was cooled to room temperature and diluted with ether. The ethereal solution was washed with an aqueous saturated sodium bicarbonate solution (2×), water, and brine and worked up as usual. The residual light yellow oil was purified by flash column chromatography (eluent PE/EA 6:1) to yield an unseparable mixture of dienes **49**.

A solution of a mixture of dienes **49** (0.50 g; 1.28 mmol) in a mixture of MeOH and CH_2Cl_2 3:1 (40 mL) was ozonolyzed at −78°C. The excess ozone was expelled and $NaBH_4$ (0.10 g; 2.56 mmol) was added at −78°C. The mixture was allowed to warm to room temperature. After stirring overnight an 1 M aqueous solution of hydrochloric acid was added. The aqueous mixture was extracted with ethyl acetate. The combined organic layers were washed with brine and worked up as usual.

The crude product was dissolved in MeOH (10 mL) and an 1 M solution of sodium methoxide in methanol (2 mL) was added. After stirring overnight at room temperature the MeOH was evaporated under reduced pressure. The residue was acidified with an 1 M aqueous solution of hydrochloric acid and extracted with CH_2Cl_2. Work up as usual afforded a residue which was flash chromatographed (eluent first EA, then EA/MeOH 95:5) to yield triol **37** (0.27 g; 0.86 mmol; 67%) as a white crystalline solid, identical with the product mentioned before.

3.7.6. (+)-(3a*R*,5*S*,5a*S*,9a*S*,9b*R*)-3a,6,6,9a-Tetramethyldodecahydronaphtho[2,1-*b*]furan-5-ol (39). A solution of triol **37** (1.0 g; 3.70 mmol) and *p*-toluenesulfonic acid (0.10 g; 0.52 mmol) in nitromethane (50 mL) was stirred at room temperature for 4 h. Ether was added and the mixture was washed with saturated aqueous sodium bicarbonate and brine and worked up as usual. Flash column chromatography on silica gel (eluent PE/EA 1:1) gave 6α-hydroxy Ambrox® (**39**) (0.60 g; 2.37 mmol; 64%) as white crystals. Mp 146–148°C; $[\alpha]_D$=+15.1 (*c* 1.1); IR (KBr) ν_{max} 3423, 2964, 2844, 1463, 1414, 1379, 1247, 1051 cm^{-1}; ^1H NMR δ 0.86 (s, 3H), 1.00 (s, 3H), 1.12 (s, 3H), 1.15 (s, 3H), 1.02–1.74 (m, 12H), 2.27 (dd, *J*=3.9, 11.1 Hz, 1H), 3.77–4.00 (m, 3H); ^{13}C NMR δ 16.7 (q), 18.6 (t), 22.1 (q), 22.9 (q), 23.0 (t), 34.1 (s), 35.8 (s), 36.7 (q), 40.3 (t), 44.4 (t), 51.7 (t), 60.3 (d), 62.8 (d), 65.7 (t), 70.9 (d), 79.1 (s); HRMS: (M^+−1), found 251.2013. $C_{16}H_{27}O_2$ requires 251.2011; MS *m/e* (%) 252 (M^+, 1), 251 (1), 237 (100), 219 (10), 125 (7), 113 (11), 109 (10), 95 (6), 69 (15), 43 (8); Anal. found C, 76.14; H, 11.18%. $C_{16}H_{28}O_2$ requires C, 76.08; H, 11.34%.

3.7.7. (+)-(1*S*,4*S*,4a*R*,8a*S*)-4((3*S*)-3-Hydroxy-3-methyl-4-pentenyl)-4a,8,8-trimethyl-3-spiro-2′-oxiran-decahydro-1-naphtalenol (42). To a stirred solution of larixol (**1**) (6.0 g; 19.61 mmol) in CH_2Cl_2 (100 mL), acetone (100 mL), H_2O (180 mL), [18]crown-6 (600 mg) and sodium hydrogen carbonate (24 g) was added a solution of oxone (18.08 g; 29.41 mmol) in H_2O (100 mL) at 0°C. After stirring at 0°C for 90 min the mixture was diluted with a saturated aqueous sodium hydrogen carbonate solution. The aqueous mixture was extracted with ethyl acetate and the combined organic layers were washed with a 10% aqueous solution of $Na_2S_2O_3$, saturated aqueous sodium bicarbonate and brine. Usual work up gave a crude oil which was purified by flash column chromatography (eluent PE/EA 1:1) to give first monoepoxide **42** (4.46 g; 13.33 mmol; 68%) as a white crystalline solid. Further elution afforded the diepoxide **41** (1.26 g; 3.73 mmol; 19%) as white crystals.

3.7.8. (+)-(1*S*,4*S*,4a*R*,8a*S*)-4((3*S*)-3-Hydroxy-3-methyl-4-spiro-2′-oxiran)-4a,8,8-trimethyl-3-spiro-2′-oxiran-decahydro-1-naphtalenol (41). Mp 74–75°C; $[\alpha]_D$=+17.7 (*c* 1.9); IR (liquid film) ν_{max} 3445, 3051, 2930, 2866, 1460, 1455, 1387, 1366 cm^{-1}; ^1H NMR δ 0.76 (s, 3H), 0.97 (s, 3H), 1.12 (s, 3H), 1.18 (s, 3H), 1.03–1.91 (m, 16H), 2.51–2.84 (m, 5H), 3.96 (dt, *J*=3.5, 11.2 Hz, 1H); ^{13}C NMR δ 15.4 (t), 15.8 (q), 18.3 (t), 22.3 (q), 22.6 (q), 33.8 (s), 36.6 (q), 39.2 (s), 40.2 (s), 42.9 (t), 43.2 (t), 43.7 (t), 47.0 (t), 51.1 (t), 53.3 (d), 57.6 (s), 58.0 (d), 60.3 (d), 69.5 (s), 69.8 (d); HRMS: M^+, found 338.2460. $C_{20}H_{34}O_4$ requires 338.2457; MS *m/e* (%) 338 (M^+, 1), 307 (43), 213 (63), 153 (48), 109 (100), 95 (79), 93 (45), 81 (63), 69 (96), 55 (62), 43 (97), 41 (51); Anal. found C, 70.90; H, 10.12%. $C_{20}H_{34}O_4$ requires C, 70.97; H, 10.12%.

42; Mp 114–115°C; $[\alpha]_D$=+16.3 (*c* 1.7); IR (KBr) ν_{max} 3442, 3048, 2932, 2857, 1455, 1237 cm^{-1}; ^1H NMR δ 0.81 (s, 3H), 0.99 (s, 3H), 1.19 (s, 3H), 1.24 (s, 3H), 0.94–2.05 (m, 16H), 2.59 (d, *J*=4.3 Hz, 1H), 2.79 (dd, *J*=1.8, 4.2 Hz, 1H), 4.01 (dt, *J*=4.8, 10.9 Hz, 1H), 5.04 (dd, *J*=1.3, 10.7 Hz, 1H), 5.20 (dd, *J*=1.3, 17.2 Hz, 1H), 5.84 (dd, *J*=10.7, 17.2 Hz, 1H); ^{13}C NMR δ 15.8 (q), 16.0 (t), 18.3 (t), 22.3 (q), 28.1 (q), 33.8 (s), 36.6 (q), 39.2 (t), 40.2 (s), 43.6 (t), 43.7 (t), 47.0 (t), 51.2 (t), 53.7 (d), 57.7 (s), 60.3 (d), 69.9 (d), 73.6 (s), 111.8 (t), 145.0 (d); HRMS: (M^+−31), found 291.2323. $C_{19}H_{31}O_2$ requires 291.2324; MS *m/e* (%) 291 [(M^+−31), 8], 233 (60), 109 (91), 69 (90), 43 (59), 31 (100); Anal. found C, 74.19; H, 10.85%. $C_{20}H_{34}O_3$ requires C, 74.49; H, 10.63%.

3.7.9. (−)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-4-Hydroxy-2,5,5,8a-tetramethyl-1-(2-oxo-ethyl)decahydro-2-naphthalenyl acetate (43). A solution of 6α-hydroxy **4** (0.30 g; 0.92 mmol) and $NaIO_4$ (1.28 g; 6.0 mmol) in THF (20 mL) and water (4 mL) was treated with a 2.5 wt% OsO_4 solution in *tert*-BuOH (0.5 mL). The mixture was warmed to 45°C and stirred overnight. The reaction mixture was filtered and diluted with a saturated aqueous Na_2SO_3 solution and extracted with ethyl acetate. The combined organic layers were dried and evaporated. Purification was performed by flash column chromatography (eluent PE/EA 1:1) to yield aldehyde **43** (0.183 g; 0.58 mmol; 63%) as a colourless oil. Further elution gave the acetyl compounds **45a** (0.044 g; 0.15 mmol; 16%) and **45b** (0.033 g; 0.11 mmol; 12%) as liquids.

43; $[\alpha]_D$=−9.6 (*c* 0.2, EtOH); IR (KBr) ν_{max} 3498, 2933, 1726, 1713, 1388, 1274, 1055 cm^{-1}; ^1H NMR δ 0.87 (s, 3H), 0.98 (s, 3H), 1.13 (s, 3H), 1.52 (s, 3H), 1.88 (s, 3H),

1.17–1.93 (m, 12H), 3.02 (dd, *J*=4.0, 12.2 Hz, 1H), 3.86 (dt, *J*=4.0, 10.9 Hz, 1H), 9.65 (t, *J*=2.2 Hz, 1H); ^{13}C NMR δ 17.1 (q), 18.0 (t), 21.5 (q), 21.9 (q), 22.5 (q), 33.6 (s), 36.3 (q), 38.3 (s), 39.9 (t), 40.4 (t), 43.2 (t), 49.6 (t), 52.7 (d), 60.3 (d), 68.3 (d), 84.0 (s), 169.7 (s), 202.0 (d); HRMS: (M^+-15), found 295.1902. $C_{17}H_{27}O_4$ requires 295.1909; MS *m/e* (%) 295 [(M^+-15), 46], 125 (8), 124 (40), 109 (100), 97 (37), 95 (44), 87 (32), 81 (39), 69 (78), 43 (87).

3.7.10. 1-((2ζ,3a*R*,5*S*,5a*S*,9a*S*,9b*R*)-5-Hydroxy-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-*b*]furan-2-yl)ethanone (45a). $[\alpha]_D$=+0.6 (*c* 0.5); IR (KBr) ν_{max} 3483, 2924, 1711, 1459, 1245, 1047 cm^{-1}; ^{1}H NMR δ 0.80 (s, 3H), 0.93 (s, 3H), 1.09 (s, 3H), 1.14 (s, 3H), 0.98–2.03 (m, 12H), 2.14 (s, 3H), 2.28 (dd, *J*=3.9, 11.1 Hz, 1H), 3.88 (dt, *J*=3.9, 10.8 Hz, 1H), 4.34 (dd, *J*=3.2, 9.8 Hz, 1H); ^{13}C NMR δ 16.2 (q), 18.1 (t), 21.6 (q), 22.8 (q), 26.8 (q), 26.9 (t), 33.7 (s), 35.3 (s), 36.2 (q), 39.8 (t), 43.9 (t), 51.1 (t), 59.1 (d), 62.1 (d), 70.2 (d), 81.2 (d), 81.8 (s), 210.8 (s); HRMS: (M^+-43), found 251.2013. $C_{16}H_{27}O_2$ requires 251.2011; MS *m/e* (%) 251 [(M^+-43), 30], 233 (79), 189 (67), 125 (34), 119 (38), 109 (45), 43 (48), 31 (100); Anal. found C, 73.06; H, 9.99%. $C_{18}H_{30}O_3$ requires C, 73.43; H, 10.27%.

3.7.11. 1-((2ζ,3a*R*,5*S*,5a*S*,9a*S*,9b*R*)-5-Hydroxy-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-*b*]furan-2-yl)ethanone (45b). $[\alpha]_D$=−5.0 (*c* 0.1); IR (KBr) ν_{max} 3470, 2926, 1717, 1459, 1385, 1058 cm^{-1}; ^{1}H NMR δ 0.79 (s, 3H), 0.89 (s, 3H), 1.05 (s, 3H), 1.09 (s, 3H), 1.02–1.99 (m, 12H), 2.17 (s, 3H), 2.26 (dd, *J*=3.9, 11.2 Hz, 1H), 3.87 (dt, *J*=7.0, 10.8 Hz, 1H), 4.28 (t, *J*=8.2 Hz, 1H); ^{13}C NMR δ 16.6 (q), 18.1 (t), 21.6 (q), 24.3 (q), 26.0 (t), 26.9 (q), 33.7 (s), 35.4 (s), 36.3 (q), 39.9 (t), 43.9 (t), 51.2 (t), 60.3 (d), 62.1 (d), 70.2 (d), 81.0 (s), 82.8 (d), 211.0 (s); HRMS: (M^+-15), found 279.1959. $C_{17}H_{27}O_3$ requires 279.1960; MS *m/e* (%) 279 [(M^+-15), 2], 233 (75), 189 (86), 125 (43), 119 (52), 109 (65), 69 (100), 43 (74); Anal. found C, 72.98; H, 9.96%. $C_{18}H_{30}O_3$ requires C, 73.43; H, 10.27%.

3.7.12. (+)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-4-(Acetyloxy)-2,5,5,8a-tetramethyl-1-(2-oxo-ethyl)decahydro-2-naphthalenyl acetate (44). This reaction was performed as described for **43**. Purification by flash column chromatography (eluent PE/EA 3:2) afforded aldehyde **44** (0.174 g; 0.49 mmol; 72%) as a white crystalline solid. Mp 114–116°C; $[\alpha]_D$=+31.2 (*c* 0.5); IR (KBr) ν_{max} 2929, 1719, 1710, 1239, 1045 cm^{-1}; ^{1}H NMR δ 0.87 (s, 3H), 0.95 (s, 3H), 1.04 (s, 3H), 1.57 (s, 3H), 1.07–1.89 (m, 11H), 1.90 (s, 3H), 2.05 (s, 3H), 2.94 (dd, *J*=4.1, 12.2 Hz, 1H), 5.14 (dt, *J*=4.1, 11.2 Hz, 1H), 9.69 (t, *J*=2.1 Hz, 1H); ^{13}C NMR δ 16.9 (q), 17.9 (t), 21.4 (q), 21.8 (q), 21.9 (q), 22.5 (q), 33.2 (s), 35.9 (q), 38.5 (s), 39.8 (t), 40.4 (t), 43.0 (t), 45.2 (t), 52.4 (d), 57.8 (d), 69.6 (d), 84.3 (s), 169.5 (s), 170.0 (s), 201.7 (d); HRMS: (M^+-15), found 337.2006. $C_{19}H_{29}O_5$ requires 337.2015; MS *m/e* (%) 337 [(M^+-15), 1], 293 (4), 233 (64), 190 (70), 109 (29), 43 (100); Anal. found C, 67.95; H, 9.15%. $C_{20}H_{32}O_5$ requires C, 68.15; H, 9.15%.

3.7.13. (+)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-4-(Acetyloxy)-2,5,5,8a-tetramethyl-1-(2-oxo-ethyl)decahydro-2-naphthalenyl acetate (44) and (+)-((1*R*,2*R*,4*S*,4a*S*,8a*S*)-2,4-Bis(acetyloxy)-2,5,5,8a-tetramethyldecahydro-1-naphthalenyl)-acetic acid (47). A stirred solution of the crude enol ether **21** (3.2 g; max. 8.12 mmol) in acetone (80 mL) was treated dropwise with Jones' reagent (20 mL; 53.44 mmol) at 0°C. Stirring was continued for 1 h and water (300 mL) was added. The aqueous mixture was extracted with ethyl acetate. The combined organic layers were washed with brine and worked up as usual to give a mixture of aldehyde **44** and acid **47** (2.73 g). A sample was purified by flash column chromatography on silica gel (eluent EA) to give crystalline **44** (26%) and oily **47** (24%). Spectral data of **44** were identical with the above mentioned.

47; $[\alpha]_D$=+45.5 (*c* 0.4); IR (KBr) ν_{max} 3437, 2929, 1740, 1709, 1244, 1134, 1033 cm^{-1}; ^{1}H NMR δ 0.85 (s, 3H), 0.93 (s, 3H), 1.02 (s, 3H), 1.56 (s, 3H), 1.89 (s, 3H), 1.11–1.95 (m, 10H), 2.04 (s, 3H), 2.33–2.42 (m, 2H), 2.88 (dd, *J*=4.0, 12.1 Hz, 1H), 5.11 (dt, *J*=4.0, 11.1 Hz, 1H); ^{13}C NMR δ 16.7 (q), 17.9 (t), 21.2 (q), 21.8 (q), 22.0 (q), 22.4 (q), 30.4 (t), 33.1 (s), 35.9 (q), 38.6 (t), 38.9 (s), 43.0 (t), 45.0 (t), 54.3 (d), 57.5 (d), 69.7 (d), 84.3 (s), 169.8 (s), 170.1 (s), 180.2 (s); HRMS: (M^+-60), found 308.1988. $C_{18}H_{28}O_4$ requires 308.1988; MS *m/e* (%) 308 [(M^+-60), 2], 266 (26), 249 (26), 248 (100), 233 (22), 188 (43), 173 (23), 119 (31), 69 (27), 43 (54).

3.7.14. (+)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-4-(Acetyloxy)-1-((3*S*)-3-(acetyloxy)-3-methyl-4-pentenyl)-2,5,5,8a-tetramethyl-decahydro-2-naphthalenyl acetate (48). 6α-Hydroxy **4** (0.50 g; 1.54 mmol) was dissolved in *N*,*N*-dimethylaniline (15 mL) and acetyl chloride (8.83 g; 112.5 mmol) was added dropwise and stirred overnight. The reaction mixture was acidified cautiously by a 4 M aqueous solution of sulfuric acid and worked up as usual. The residual yellow oil was purified by flash column chromatography on silica gel (eluent PE/EA 3:1) to yield triacetate **48** (0.57 g; 1.23 mmol; 80%) as white crystals. Mp 100–102°C; $[\alpha]_D$=+38.8 (*c* 2.2); IR (KBr) ν_{max} 3441, 2931, 1737, 1732, 1372, 1258, 1239, 1021 cm^{-1}; ^{1}H NMR δ 0.81 (s, 3H), 0.88 (s, 3H), 0.97 (s, 3H), 1.49 (s, 3H), 1.01–1.92 (m, 16H), 1.93 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.74 (dd, *J*=4.1, 12.0 Hz, 1H), 5.03 (dt, *J*=4.1, 11.0 Hz, 1H), 5.07 (dd, *J*=0.9, 17.5 Hz, 1H), 5.15 (dd, *J*=0.9, 10.7 Hz, 1H), 5.92 (dd, *J*=10.9, 17.5 Hz, 1H); ^{13}C NMR δ 16.6 (q), 17.9 (t), 19.4 (t), 21.7 (q), 21.8 (q), 21.9 (q), 22.1 (q), 22.7 (q), 23.6 (q), 33.1 (s), 35.9 (q), 39.4 (t), 39.4 (s), 42.1 (t), 43.3 (t), 44.9 (t), 57.7 (d), 57.9 (d), 70.0 (d), 83.0 (s), 85.8 (s), 113.2 (t), 141.7 (d), 169.7 (s), 169.9 (s), 170.1 (s); HRMS: M^+, found 450.2977. $C_{26}H_{42}O_6$ requires 450.2981; MS *m/e* (%) 450 (M^+, 1), 435 (1), 270 (68), 262 (63), 202 (69), 190 (88), 189 (100), 43 (83); Anal. found C, 69.07; H, 9.48%. $C_{26}H_{42}O_6$ requires C, 69.30; H, 9.40%.

3.7.15. (+)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-4-(Acetyloxy)-1-((3*E*)-5-(acetyloxy)-3-methyl-3-pentenyl)-2,5,5,8a-tetramethyl-decahydro-2-naphthalenyl acetate (50). A mixture of triacetate **48** (1.0 g; 2.22 mmol) and $PdCl_2(CH_3CN)_2$ (25 mg; 0.10 mmol) in freshly distilled THF (25 mL) was stirred at room temperature for 1 h. Ether was added and the mixture was washed with brine and worked up as usual. Flash column chromatography (eluent PE/EA 6:1) gave **50** (0.98 g; 2.18 mmol; 98%) as a sticky solid. Mp 58–61°C; $[\alpha]_D$=+38.2 (*c* 2.5); IR (KBr) ν_{max} 3443, 2931, 1735, 1367, 1025 cm^{-1}; ^{1}H NMR δ 0.78 (s, 3H), 0.81 (s, 3H), 0.94 (s, 3H), 1.47 (s, 3H), 1.65 (s, 3H), 1.12–1.87 (m, 13H), 1.88 (s,

3H), 1.95 (s, 3H), 2.00 (s, 3H), 2.72 (dd, J=4.1, 12.0 Hz, 1H), 4.52 (d, J=7.1 Hz, 2H), 5.04 (dt, J=4.1, 11.1 Hz, 1H), 5.27 (dt, J=1.2, 7.2 Hz, 1H); ^{13}C NMR δ 16.0 (q), 16.5 (q), 17.9 (t), 21.0 (q), 21.7 (q), 21.8 (q), 21.9 (q), 22.7 (q), 24.2 (t), 33.5 (s), 35.9 (q), 38.2 (t), 39.1 (t), 39.6 (s), 43.4 (t), 44.1 (t), 55.2 (d), 57.5 (d), 61.3 (t), 73.2 (d), 118.2 (d), 142.6 (s), 144.1 (s), 169.9 (s), 170.0 (s), 171.0 (s); HRMS: (M^+−60), found 390.2767. $C_{24}H_{38}O_4$ requires 390.2770; MS *m/e* (%) 390 [(M^+−60), 1], 330 (6), 270 (12), 190 (100), 140 (34), 119 (19), 81 (11), 69 (10).

3.7.16. (+)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-4-(Acetyloxy)-2,5,5,8a-tetramethyl-1-(3-oxobutyl)decahydro-2-naphthalenyl acetate (51). A solution of compound **50** (2.0 g; 4.44 mmol) in a mixture of CH_2Cl_2 and MeOH 1:1 (60 mL) was ozonolyzed at −78°C. The excess ozone was expelled and PPh_3 (2.33 g; 8.88 mmol) was added at −78°C. The mixture was allowed to warm up to room temperature. After stirring overnight the solvents were evaporated and the residue was purified by flash column chromatography (eluent PE/EA 3:1) to yield **51** (1.6 g; 4.22 mmol; 95%) as a white solid. Mp 128–129°C; $[\alpha]_D$=+42.8 (*c* 1.1); IR (KBr) ν_{max} 3433, 2931, 1722, 1708, 1369, 1248, 1025 cm^{-1}; ^{1}H NMR δ 0.81 (s, 3H), 0.90 (s, 3H), 0.97 (s, 3H), 1.51 (s, 3H), 1.21–1.85 (m, 12H), 1.90 (s, 3H), 2.01 (s, 3H), 2.07 (s, 3H), 2.51 (dd, J=7.0, 10.5 Hz, 1H), 2.74 (dd, J=4.1, 12.1 Hz, 1H), 5.06 (dt, J=4.1, 11.0 Hz, 1H); ^{13}C NMR δ 16.5 (q), 17.9 (t), 19.4 (t), 21.7 (q), 21.9 (q), 22.0 (q), 22.8 (q), 29.9 (q), 33.2 (s), 35.9 (q), 39.4 (s), 39.6 (t), 43.2 (t), 44.9 (t), 46.2 (t), 57.1 (d), 57.8 (d), 69.9 (d), 85.9 (s), 169.9 (s), 170.0 (s), 208.8 (s); HRMS: (M^+−60), found 320.2334. $C_{20}H_{32}O_3$ requires 320.2351; MS *m/e* (%) 320 [(M^+−60), 4], 260 (100), 242 (23), 202 (58), 189 (69), 187 (55), 153 (25), 119 (54), 43 (34); Anal. found C, 69.52; H, 9.68%. $C_{22}H_{36}O_5$ requires C, 69.44; H, 9.54%.

3.7.17. (+)-(1*R*,2*R*,4*S*,4a*S*,8a*S*)-4-(Acetyloxy)-1-(2-(acetyloxy)ethyl)-2,5,5,8a-tetramethyldecahydro-2-naphthalenyl acetate (52). Methyl ketone **51** (0.20 g; 0.52 mmol) and *m*-CPBA (0.18 g; 1.04 mmol) in CH_2Cl_2 (25 mL) were stirred at room temperature for 1 week. Ether was added and the mixture was washed with a 2% aqueous solution of $Na_2S_2O_3$, saturated aqueous sodium bicarbonate and brine, respectively, and worked up as usual. Flash column chromatography (eluent PE/EA 6:1) of the residual oil gave triacetate **52** (0.17 g; 0.42 mmol; 83%) as white crystals. Mp 142–144°C; $[\alpha]_D$=+25.4 (*c* 0.9); IR (KBr) 3428, 2934, 1729, 1718, 1706, 1239, 1026 cm^{-1}; ^{1}H NMR δ 0.82 (s, 3H), 0.90 (s, 3H), 0.99 (s, 3H), 1.53 (s, 3H), 1.18–1.86 (m, 11H), 1.92 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.80 (dd, J=4.1, 12.1 Hz, 1H), 3.94–4.18 (m, 2H), 5.08 (dt, J=4.1, 11.2 Hz, 1H); ^{13}C NMR δ 16.7 (q), 17.9 (t), 21.6 (q), 21.9 (2×q), 22.0 (q), 22.8 (q), 24.8 (t), 33.2 (s), 35.9 (q), 39.0 (s), 39.4 (t), 43.2 (t), 44.9 (t), 54.0 (d), 57.8 (d), 65.6 (t), 69.8 (d), 85.2 (s), 169.9 (s), 170.0 (s), 171.0 (s); HRMS: (M^+−60), found 336.2296. $C_{20}H_{32}O_4$ requires 336.2301; MS *m/e* (%) 336 [(M^+−60), 1], 276 (30), 217 (19), 216 (68), 201 (35), 189 (21), 119 (20), 109 (20), 69 (25), 43 (100); Anal. found C, 66.99; H, 9.30%. $C_{22}H_{36}O_6$ requires C, 66.64; H, 9.15%.

3.7.18. (−)-(3a*R*,5a*S*,9a*R*,9b*R*)-3a,6,6,9a-Tetramethyldecahydronaphtho[2,1-*b*]furan-5(2*H*)-one (53). 6α-Hydroxy Ambrox® (**39**) (0.30 g; 1.19 mmol) in acetone (10 mL) was treated with Jones' reagent (2 mL; 5.34 mmol) at 0°C. After 1 h the excess of Jones' reagent was destroyed by adding *i*-PrOH (3 mL) and the mixture was diluted with water (150 mL). Extraction with ethyl acetate, followed by usual work up gave after flash column chromatography on silica gel (eluent PE/EA 5:1) ketone **53** (0.27 g; 1.08 mmol; 91%) as a crystalline solid. Mp 66–68°C; $[\alpha]_D$=−34.1 (*c* 1.3); IR (KBr) ν_{max} 3412, 2927, 1705, 1451, 1388, 1361, 1267 cm^{-1}; ^{1}H NMR δ 0.88 (s, 3H), 0.96 (s, 3H), 1.06 (s, 3H), 1.13 (s, 3H), 1.09–1.94 (m, 8H), 2.13 (dd, J=6.2, 13.0 Hz, 2H), 2.65 (dd, J=6.2, 17.3 Hz, 2H), 3.95–4.07 (m, 2H); ^{13}C NMR δ 15.9 (q), 18.0 (t), 21.3 (q), 21.5 (q), 22.2 (t), 32.2 (s), 32.2 (q), 36.8 (s), 40.3 (t), 42.8 (t), 58.0 (t), 60.0 (d), 65.4 (t), 66.9 (d), 81.0 (s), 209.4 (s); HRMS: M^+, found 250.1935. $C_{16}H_{26}O_2$ requires 250.1933; MS *m/e* (%) 250 (M^+, 12), 236 (14), 235 (100), 151 (15), 123 (16), 111 (23), 109 (16), 43 (12); Anal. found C, 77.17; H, 10.74%. $C_{16}H_{26}O_2$ requires C, 76.75; H, 10.47%.

3.7.19. (+)-(3a*R*,5*S*,5a*S*,9a*S*,9b*R*)-3a,6,6,9a-Tetramethyldodecahydronaphtho[2,1-*b*]furan-5-yl acetate (54). A solution of 6α-hydroxy Ambrox® (**39**) (0.30 g; 1.19 mmol) in dichloromethane (10 mL) and pyridine (5 mL) was treated with acetic anhydride (0.5 mL; 0.54 g; 5.32 mmol) and DMAP (25 mg; 0.20 mmol). After 2 h the reaction mixture was neutralized with a 4 M solution of hydrochloric acid. Usual work up gave the crude product which was purified by flash column chromatography (eluent PE/EA 5:1) to give acetate **54** (0.33 g; 1.12 mmol; 94%) as white crystals. Mp 73–74°C; $[\alpha]_D$=+23.9 (*c* 1.2); IR (liquid film) ν_{max} 2927, 2875, 1738, 1378, 1242, 1030 cm^{-1}; ^{1}H NMR δ 0.89 (s, 3H), 0.94 (s, 3H), 1.00 (s, 3H), 1.19 (s, 3H), 1.08–1.81 (m, 11H), 2.05 (s, 3H), 2.20 (dd, J=4.1, 11.2 Hz, 1H), 3.79–4.00 (m, 2H), 5.19 (dt, J=4.1, 11.2 Hz, 1H); ^{13}C NMR δ 16.1 (q), 18.1 (t), 21.7 (q), 21.9 (q), 22.3 (q), 22.5 (t), 33.2 (s), 35.2 (s), 35.8 (q), 39.8 (t), 43.7 (t), 43.7 (t), 59.5 (d), 59.8 (d), 65.3 (t), 71.6 (d), 78.4 (s), 170.1 (s); HRMS: (M^+−15), found 279.1957. $C_{17}H_{27}O_3$ requires 279.1960; MS *m/e* (%) 294 (M^+, 1), 279 (1), 220 (16), 219 (100), 123 (10), 69 (6), 43 (14); Anal. found C, 73.11; H, 10.30%. $C_{18}H_{30}O_3$ requires C, 73.43; H, 10.27%.

3.7.20. (+)-(3a*R*,5*S*,5a*S*,9a*S*,9b*R*)-3a,6,6,9a-Tetramethyldodecahydronaphtho[2,1-*b*]furan-5-yl methyl ether (55). A 60% suspension of sodium hydride in mineral oil (0.08 g; 2.0 mmol) and 6α-hydroxy Ambrox® (**39**) (0.10 g; 0.397 mmol) in dry DMF (15 mL) was heated at 100°C under nitrogen for 1 h. Iodomethane (0.86 mL; 1.97 mmol) was added dropwise and the mixture was heated overnight. The mixture was cooled, poured into water and acidified with a 4 M solution of hydrochloric acid and the mixture was worked up as usual. Flash column chromatography with PE/EA 3:1 as the eluent gave ether **55** (0.10 g; 0.377 mmol; 95%) as a colourless oil. $[\alpha]_D$=+41.9 (*c* 0.2); IR (liquid film) ν_{max} 3372, 2929, 2877, 1724, 1462, 1455, 1380, 1098 cm^{-1}; ^{1}H NMR δ 0.89 (s, 3H), 0.92 (s, 3H), 1.11 (s, 3H), 1.14 (s, 3H), 1.08–1.80 (m, 11H), 2.44 (dd, J=3.8, 11.3 Hz, 1H), 3.35 (s, 3H), 3.87 (dt, J=3.9, 10.7 Hz, 1H), 3.85–3.97 (m, 2H); ^{13}C NMR δ 16.5 (q), 18.2 (t), 22.0 (q), 22.6 (q), 22.7 (t), 33.6 (s), 35.2 (s), 36.1 (q), 39.9

(t), 43.8 (t), 45.0 (t), 56.2 (q), 59.9 (d), 60.7 (d), 65.3 (t), 78.6 (s), 79.8 (d); HRMS: (M^+-15), found 251.2014. $C_{16}H_{27}O_2$ requires 251.2011; MS *m/e* (%) 266 (M^+, 3), 251 (33), 219 (11), 109 (7), 101 (20), 85 (10), 84 (100), 43 (12), 31 (9).

3.7.21. (−)-(3a*R*,9a*R*,9b*R*)-3a,6,6,9a-Tetramethyl-1,2,3a,4,6,7,8,9,9a,9b-decahydronaphtho[2,1-*b*]furan (56). To a stirred mixture of 6α-hydroxy Ambrox® (**39**) (0.05 g; 0.20 mmol) in pyridine (5 mL) was added thionyl chloride (5 mL; 8.16 g; 68.5 mmol) at 0°C. The mixture was allowed to come to room temperature and stirring was continued overnight. The reaction mixture was quenched with ice-water and the aqueous mixture was extracted with ethyl acetate and usual work up afforded a yellow oil which was purified by flash column chromatography on silica gel (eluent PE/EA 15:1) to yield odorous compound **56** (0.027 g; 0.115 mmol; 57%) as a colourless oil. $[\alpha]_D=-70.0$ (*c* 0.4); IR (KBr) ν_{max} 3420, 2926, 1468, 1377, 1165, 1048 cm^{-1}; ^1H NMR δ 1.07 (s, 3H), 1.10 (s, 3H), 1.13 (s, 3H), 1.14 (s, 3H), 1.16–1.94 (m, 9H), 2.26 (d, *J*=4.0 Hz, 2H), 3.94 (m, 2H), 5.45 (t, *J*=4.0 Hz, 1H); ^{13}C NMR δ 18.3 (t), 19.5 (q), 21.8 (q), 23.4 (t), 28.9 (q), 33.2 (q), 36.2 (s), 38.3 (s), 41.4 (t), 41.9 (t), 42.2 (t), 57.2 (d), 65.4 (t), 78.3 (s), 117.5 (d), 149.8 (s); HRMS: M^+, found 234.1981. $C_{16}H_{26}O$ requires 234.1984; MS *m/e* (%) 234 (M^+, 23), 219 (54), 151 (13), 150 (98), 135 (100), 105 (12), 91 (11), 43 (18).

3.7.22. (+)-(3a*R*,5*S*,5a*S*,9a*S*,9b*R*)-3a,6,6,9a-Tetramethyl-dodecahydronaphtho[2,1-*b*]furan-5-yl methanesulfonate (59). To a stirred solution of 6α-hydroxy Ambrox® (**39**) (0.30 g; 1.19 mmol) in pyridine (10 mL) was added MsCl (0.16 g; 0.11 mL; 1.42 mmol) at 0°C. The mixture was allowed to warm to room temperature and stirring was continued for 1 h. The reaction mixture was neutralized with a 4 M solution of hydrochloric acid and diluted with ether. The organic layer was washed with saturated aqueous sodium bicarbonate solution and worked up as usual. Purification of the residue by flash column chromatography (eluent PE/EA 3:1) gave **59** (0.36 g; 1.09 mmol; 92%) as a white crystalline solid. Mp 114–115°C; $[\alpha]_D=+12.7$ (*c* 1.3); IR (KBr) ν_{max} 3431, 2929, 1344, 1168, 954, 943 cm^{-1}; ^1H NMR δ 0.95 (s, 3H), 1.05 (s, 3H), 1.10 (s, 3H), 1.20 (s, 3H), 1.24–1.92 (m, 11H), 2.61 (dd, *J*=4.0, 11.0 Hz, 1H), 3.05 (s, 3H), 3.81–4.02 (m, 2H), 5.01 (dt, *J*=4.1, 11.2 Hz, 1H); ^{13}C NMR δ 16.2 (q), 17.9 (t), 21.3 (q), 22.4 (q), 22.5 (t), 33.4 (s), 35.6 (q), 35.8 (s), 40.0 (q), 40.3 (t), 44.0 (t), 47.9 (t), 59.6 (q), 60.2 (d), 65.5 (t), 78.2 (s), 80.6 (d); HRMS: M^+, found 330.1869. $C_{17}H_{30}O_4S$ requires 330.1865; MS *m/e* (%) 330 (M^+,1), 220 (16), 219 (100), 75 (21), 73 (19), 69 (16), 43 (16); Anal. found C, 61.45; H, 9.20%. $C_{17}H_{30}O_4S$ requires C, 61.78; H, 9.15%.

3.7.23. (−)-(3a*R*,9a*R*,9b*R*)-3a,6,6,9a-Tetramethyl-1,2,3a,4,6,7,8,9,9a,9b-decahydronaphtho[2,1-*b*]furan (56). The above mentioned mesylate **59** (0.025 g; 0.075 mmol) in toluene (5 mL) was purged through with nitrogen and MgI_2 (0.042 g; 0.15 mmol) was added quickly. After stirring for 150 min the mixture was diluted with ether and washed with a 2% aqueous solution of $Na_2S_2O_3$ and brine and worked up as usual. Flash column chromatography (eluent PE/EA 15:1) yielded **56** (0.012 g; 0.050 mmol; 67%) as an odorous, colourless oil, with spectral data in accordance with the above mentioned.

A mixture of mesylate **59** (0.025 g; 0.075 mmol), Li_2CO_3 (34 mg; 0.43 mmol) and LiBr (34 mg; 0.39 mmol) in dry DMF (7 mL) was heated to 120°C under nitrogen for 4 h. The mixture was cooled and water was added. The aqueous mixture was extracted with light petroleum ether and worked up as usual. The crude oil was purified by flash column chromatography (eluent PE/EA 15:1) to give fragrance compound **56** (0.013 g; 0.053 mmol; 71%) as an odorous colourless oil with spectral data in agreement with the above mentioned.

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