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SYNTHESIS OF 3α-HYDROXY-5β,10β-EPOXYCHILIOLIDE, AN EUDESMANE-EUDESMANE DERIVATIVE FROM CHILIOTRICHIUM ROSMARINIFOLIUM

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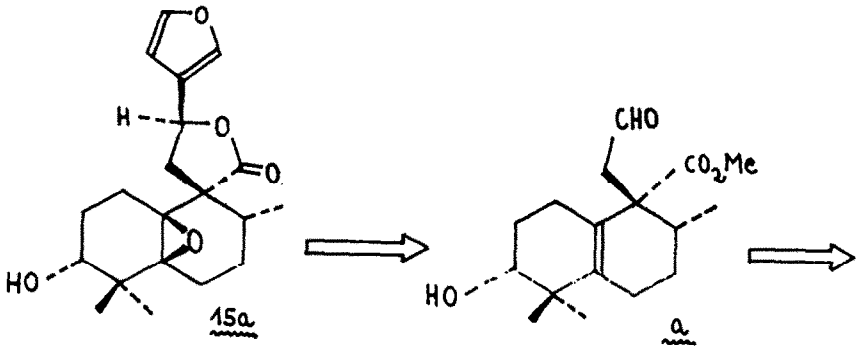
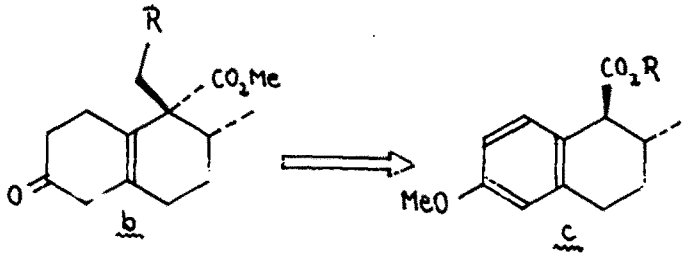
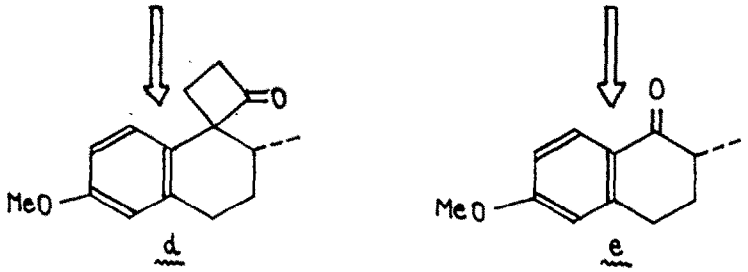
Abstract - Starting with 6-methoxytetralone the unusual diterpene 3α-hydroxy-5β,10β-epoxychiliolide (15a) has been synthesized via methyl-[1α,2α]-1',2,3,4,5,6,7,8-octahydro-6-oxo-1-(2-propenyl)-2,5,5-trimethyl-1-naphthoate (9) which by boranate reduction gave the desired α-hydroxy derivative. Oxidative degradation of the propenyl side chain afforded the aldehyde 11a which could be transformed to the racemic furan diterpene 15a by reaction with 3-lithiumfuran followed by lactonization and epoxidation. Similar the epimeric compounds 15b, 15c and 15d were synthesized which allowed a final proof of the proposed relative stereochemistry of the six chiral centres of the natural compound.

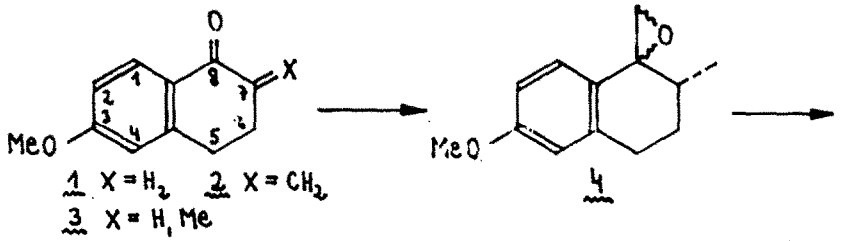
The South American Compositae Chiliotrichium rosmarinifolium contains several unusual diterpenes, its structure being elucidated by high field ^{1}H NMR spectroscopy[1]. However, due to the limited amount of material the final proof of the configuration of the epoxide in the diterpene 15a was not possible. We therefore have decided to solve this problem by synthesis of the racemic diterpene. Retrosynthetic considerations indicated that the readily available tetralone e might be an useful starting material. Transformation to the ketoester b should be possible via the intermediate c or d. Introduction of a suitable substituent in α-position to the ester group would lead to b where R could be a protected aldehyde group or a precursor which finally would allow to prepare the aldehyde a. The latter then had to be reacted with 3-lithiumfuran followed by lactonization and epoxidation, to give the direct precursor a of the diterpene 15a.

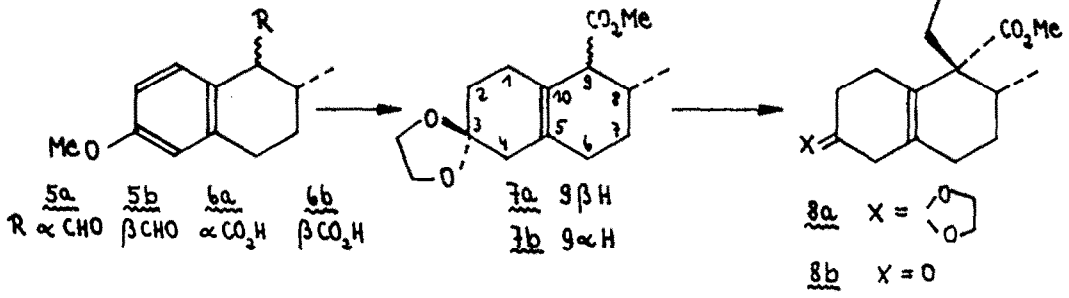
Though different ways for a synthesis of cyclobutanones are described in[2,3] the tetralone e could not be transformed to the cyclobutanone d. However, the second possibility was successful. The necessary starting material 3 was prepared by Mannich reaction of 1 with TAMA[4] (N-methyl-anilinium-trifluoro acetate) and p-formaldehyde followed by hydrogenation of the exomethylene bond affording the α-methyltetralone 3 in high yield together with small amounts of the isomeric Diels-Alder products of 2. Introduction of the carboxyl group caused some difficulties. Formation of the corresponding conjugated nitrile could be achieved in high yield. But hydrolysis and hydrogenation gave no satisfactory yields of 6a. Wittig reaction of 3 with methoxymethylene phosphorane also was unsuccessful. However, Trost epoxidation[5] and isomerization of the resulting epoxide with BF_3 etherate yielded the epimeric aldehydes 5a and b in high yield. Small amounts of 17 most likely are formed by reaction of the adduct 4a with 4

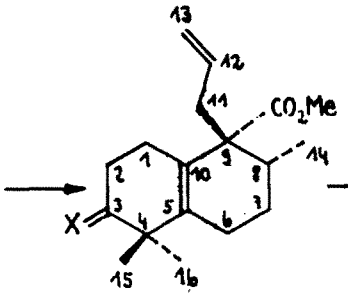

H
O
O
O
HO
15a
CHO
CO_2Me
HO
a


R
CO_2Me
O
b
CO_2R
MeO
c

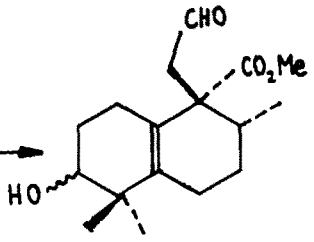

O
MeO
d
O
MeO
e


O
X
MeO
1 X = H_2 2 X = CH_2
3 X = H, Me
O
MeO
4

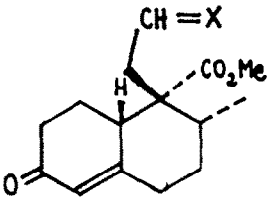

R
MeO
5a 5b 6a 6b
R ∝ CHO βCHO ∝CO_2H βCO_2H
CO_2Me
O
O
7a 9βH
7b 9∝H
CO_2Me
X
8a X =
8b X = O



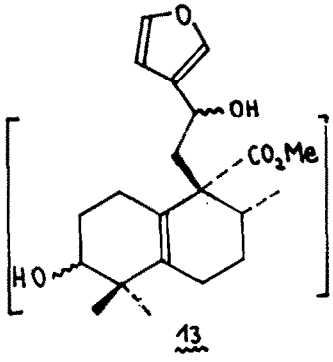
9 10a 10b
X =O ∝OH,H βOH,H



11a 3∝OH
11b 3β OH



12a X = CH_2
12b X = O



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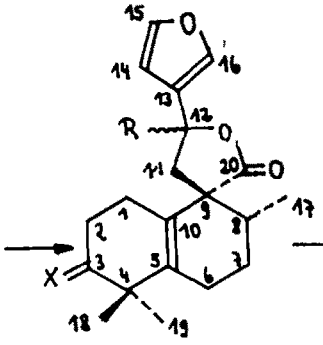
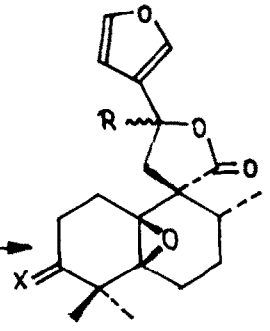
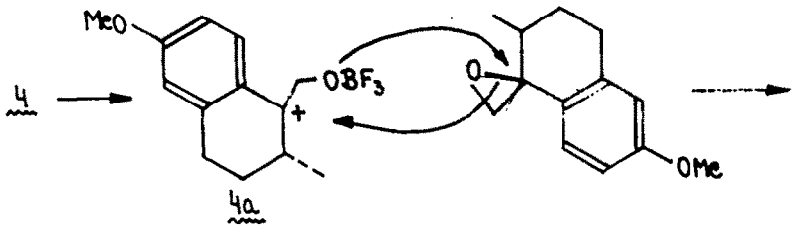




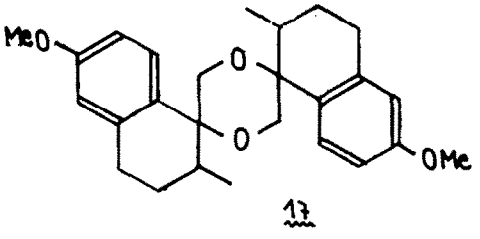
14a 14b 14c 14d
X ∝OH,H ∝OH,H βOH,H βOH,H
R ∝H βH ∝H βH

15a 15b 15c 15d
X ∝OH,H ∝OH,H βOH,H βOH,H
R ∝H βH ∝H βH

16 X=O, R=∝H



4a



17

Table 1. ^{1}H NMR spectral data of 10a, 10b, 11a and 11b (400 MHz, $CDCl_3$, δ-values in parenthesis J [Hz])

H	10a	10b	11a	11b
3	3.44 dd (10.5, 3.5)	3.50 dd (4.5, 2)	3.35 dd (11.5, 3.5)	3.55 dd (4.5, 2)
11	2.59 br dd (15, 5.5)	2.64 br dd 15, 7.5)	2.77 dd (16, 2.5)	2.92 dd (16, 2)
11'	2.45 br dd (15, 8.5)	2.46 br dd (15, 7)	2.63 dd (16, 3.5)	2.81 dd (16, 3.5)
12	5.46 dddd (17, 10, 8.5, 5.5)	5.58 dddd (17, 10, 7.5, 7)	9.49 dd (3.5, 2.5)	9.62 dd (3.5, 2)
13	5.08 br d (17)	5.13 br d (17)	-	-
13'	5.03 br d (10)	5.05 br d (10)	-	-
14	0.82 d (7)	0.85 d (7)	0.83 d (7)	0.90 d (6)
15	1.00 s	1.04 s	1.02 s	1.01 s
16	1.06 s	1.05 s	1.06 s	0.93 s
OCH_3	3.64 s	3.65 s	3.61 s	3.67 s

Table 2. ^{1}H NMR spectral data of 14a - d, 15a - d and 16 (400 MHz, $CDCl_3$, δ-values)

H	14a	14b	14c	14d	15a[a]	15b[a]	15c[b]	15d[b]	16	multiplicity
3	3.50	3.48	3.61	3.60	3.65	3.55	3.33[c]	3.31[c]	-	dd
8	1.49	1.95	2.00	2.03	1.61	1.80	1.61	1.80	1.69 ddq	m
11	2.70	2.55	2.74	2.47	2.87	2.66	2.92	2.73	2.94	dd
11'	2.18	2.36	2.19	2.38	2.16	2.40	2.19	2.43	2.25	dd
12	5.42	5.42	5.46	5.41	5.46	5.43	5.51	5.46	5.53	dd
14	6.42	6.42	6.41	6.45	6.41	6.42	6.42	6.46	6.42	dd
15	7.44	7.44	7.44	7.43	7.40	7.46	7.46	7.47	7.46	dd
16	7.46	7.47	7.45	7.47	7.47	7.49	7.48	7.50	7.48	dd
17	1.04	1.10	1.03	1.07	0.92	1.05	0.92	1.08	0.97	d
18	1.09	1.10	1.03	1.09	1.02	1.06	1.08	1.11	1.22	s
19	1.02	1.06	1.07	1.08	1.12	1.11	1.22	1.21	1.23	s

[a] in C_6D_6 (15b in parenthesis): 1.70 (1.75)(ddd, H-1α), 1.83 (1.86)(ddd, H-1β), 1.40 (1.47) (dddd, H-2α), 1.30 (1.19)(dddd, H-2β), 3.62 (3.51)(dd, H-3), 1.98 (2.01)(ddd, H-6α), 1.60 (1.65)(ddd, H-6β), 2.20 (2.01)(dddd, H-7α), 1.10 (1.10)(dddd, H-7β), 1.50 (1.64)(ddq, H-8);
[b] in C_6D_6 (15d in parenthesis): 1.84 (1.88)(ddd, H-6α), 1.56 (1.60)(ddd, H-6β), 2.13 (1.93) (dddd, H-7α), 1.04 (1.02) (dddd, H-7β), 1.40 (1.56) (ddq, H-8); [c] br s;

J [Hz]: 8,17 = 7; 11,11' = 14.5; 11,12 = 8; 14,15 = 1.5; 14,16 = 1; compounds 14a/b: 2α,3 = 11; 2β,3 = 3.5; compound 14c: 2α,3 = 2; 2β,3 = 6.5; compound 14d: 2α,3 = 3; 2β,3 = 9.5; compounds 15a/b: 1α,1β = 6α,6β = 14.5; 1α,2α = 8; 1α,2β = 2; 1β,2α = 11.5; 1β,2β = 8; 2α,2β = 6α,7β = 7α,7β = 7β,8 = 13; 6β,7α = 2; 6β,7β = 6; 7α,8 = 3; compounds 15c/d: 6α,6β = 15; 6α,7β = 7α,7β = 13; 6β,7α = 1.5; 6β,7β = 6.5; 7α,8 = 3; 7β,8 = 12; 2α,3 = 2β,3 = 2.

(s. Scheme).

Again the oxidation of the aldehyde group caused difficulties as pyridine dichromate in DMF[6] or potassium permanganate in tert. -butanol[7] only gave 3, obviously formed by oxidation of the corresponding enol. Best results were obtained by Jones oxidation[8] but still also 3 was obtained. Birch reduction of 6a and b followed by hydrolysis of the enol ether, esterification and ketalization gave the epimeric esters 7a and b which both gave the ketal 8a on alkylation with LDA and allyl bromide. Hydrolysis of the ketal with diluted sulfuric acid on silica gel gave in a 72% overall yield the corresponding ketone 8b which was transformed to the epimeric alcohols 10a and b by alkylation followed by boranate reduction (ca. 5 : 1) while reduction with L-selectride gave a 1 : 2 mixture of the alcohols. Oxidative degradation of 10a/b with osminium tetroxide/N-methyl morpholine-N-oxide followed by reaction with sodium periodate gave the aldehydes 11a and b. Similar hydrolysis of 8a with hydrochloric acid in methanol and oxidative degradation gave the conjugated ketone 12b which was useful for a X-ray analysis which established the proposed configurations at C-7 and C-8 in all compounds with the corresponding quarternary centre (s. picture). Reaction of 11a and b with 3-lithiofuran afforded after lactonization 14a - d which by epoxidation gave the isomeric diterpenes 15a - 15d. The ^{1}H NMR spectrum of the first one was identical with that of the natural compounds. As expected the reaction of 11a and b, respectively, gave a mixture of epimers at C-12, but the relative stereochemistry at C-3, C-5 and C-10 still had to be solved. From the ^{1}H NMR spectrum of 15a a quasi-equatorial orientation of the 3-hydroxy group could be deduced. Due to the presence of two sp^2 carbons two conformers are likely. However, inspection of models indicated that this could be explained with an α-hydroxy- as well as with a β-hydroxy group. As only one epoxide was obtained with both isomers a β-orientation of the epoxy group was more likely. Inspection of the IR spectra clearly showed that in the case of 15c and 15d a hydrogen bridge between 3-OH and the epoxide oxygen was present. Accordingly, in these isomers β-hydroxy groups at C-3 were present. Oxidation of 15a with pyridine chlorochromate afforded a ketone 16 which on reduction with sodium boranate gave only one isomer, the 3β-hydroxy derivative 15c. Thus the stereochemistry of the natural diterpene only differed at C-3 and not at C-5 and C-10 from 15c. As inspection of a model clearly showed that the boranate attack of 16 was favoured from the α-face the relative configuration of all isomeric diterpenes was settled.

EXPERIMENTAL

IR spectra were recorded in $CHCl_3$ or CCl_4 on a Beckman IR 4230 instrument, the NMR spectra on a Bruker WM 400 and EIMS were obtained at 70 eV with a Varian MAT 711. TLC was performed on sigel, PF 254, CC on sigel (Ø 0.16 - 0.3 mm) or with medium pressure chromatography (MPC) on sigel (Ø 30 - 60 μ).

3,4-Dihydro-6-methoxy-2-methyl-1(2H)-naphthalenone (3). 50 g (0.284 mol) 6-methoxy-tetralone, 25.6 g paraformaldehyde and 21 g (0.096 mol) TAMA in 600 ml dioxane were heated for 2 h under reflux. After addition of water the reaction product was extracted with ether. The extract was solved in 200 ml methanol and stirred with 6 g Raney-nickel and hydrogen for 1 d. After filtration and evaporation distillation afforded 43.2 g 3, bp. 108°/0.05 h Pa; colourless crystals, mp. 29° (Et_2O/petroleum ether). - ^{1}H NMR ($CDCl_3$): δ 7.99 (d, H-1, J = 8.5 Hz), 6.79 (dd, H-2, J = 8.5, 2.5), 6.65 (d, H-4, J = 2.5), 2.99 and 2.91 (m, H-5), 2.16 and 1.85 (m, H-6), 2.53 (m, H-7), 1.24 (d, H-9, J = 7), 3.83 (s, OCH_3). - Anal. calcd. for $C_{12}H_{14}O_2$: C, 75.69; H, 7.42; Found: C, 75.83; H, 7.34%. - From the undistilled part 4 g of the isomeric diene adducts were obtained. ^{1}H NMR ($CDCl_3$, spiroether): δ 7.30 (d, J = 8 Hz), 6.64 (dd,

J = 8, 2.5), 6.65 (d, J = 2.5), 8.03 (d, J = 8.5), 6.86 (dd, J = 8.5, 2.5), 6.71 (d, J = 2.5), 3.77 (s, 3H), 3.87 (s, 3H), 3.2 - 1.9 (m, 12H) and the isomer: δ 7.98 (d, J = 8.5), 7.03 (dd, J = 8.5, 2.5), 6.69 (d, J = 2.5), 7.96 (d, J = 8.5), 7.00 (dd, J = 8.5, 2.5), 6.67 (d, J = 2.5), 3.86 (s, 3H), 3.87 (s, 3H), 3.66 and 3.44 (d, J = 11.5), 3.15 - 1.4 (m, 10H).

6-Methoxy-2-methyl-1,2,3,4-tetrahydro-1α- and 1β-naphthoic acid (6a and 6b). 20 g 3 (0.105 mol) in 100 ml DMSO was added at 0° to the ylene prepared from 24.5 g (0.120 mol) trimethylsulfonium iodide in 500 ml DMSO and 2.9 g NaH (0.120 mol). After stirring for 15 h at room temperature water and ice were added and the product was extracted with ether. To the crude product (21.5 g) in 200 ml benzene at 0° 1 ml borontrifluoride etherate was added. After 10 min. the solution was concentrated to about 50 ml and 1 l acetone was added. To the stirred solution at 0° 30 ml of Jones reagent[8] was added. After addition of ether and 5 ml methanol the solution was filtered over silica gel and evaporated. The acid fraction (25.14 g) (57%) was a crystalline mixture of 6a and 6b. TLC (Et_2O/petroleum ether, 9 : 1) gave 6a, mp 120° (Et_2O/petroleum ether) and 6b, mp. 145° (Et_2O/petroleum ether). From the neutral part 0.7 g (3%) of 17, mp. 218° (Et_2O) was obtained.

6a: Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32; Found: C, 70.74; H, 7.38%.

6b: Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32; Found: C, 70.81; H, 7.27%.

17: Calcd. for $C_{24}H_{24}O_4$: C, 76.43; H, 7.90; Found: C, 76.28; H, 7.64%. - ^{1}H NMR ($CDCl_3$): 6a/b: δ 7.10 (d, H-1, J = 8.5 Hz), 6.72 (dd, H-2, J = 8.5, 2), 6.67 (d, H-4, J = 2), 3.73 (d, H-7, J = 5) and 3.42 (d, H-7 (6b), J = 8.5), 1.15)1.12) (d, H-9, J = 6.5), 3.77 (s, OCH_3); 17: δ 8.20 (d, J = 8.5 Hz), 6.78 (dd, J = 8, 2.5), 6.72 (d, J = 2.5), 3.70 and 4.00 (d, J = 12), 3.83 (s, 3H), 2.87 (dd, J = 18, 8, 3.5), 2.80 (ddd, J = 18, 10.5, 6.5), 2.57 (dddd, J = 13, 10.5, 8.5, 4.5), 2.12 (ddq, J = 7, 4.5, 3.5), 1.48 (ddt, J = 13, 6.5, 3.5), 0.71 (d, J = 7, 3H); ^{13}C NMR: δ 158.7 s, 139.4 s, 131.3 d, 127.7 s, 113.9 d, 110.5 d, 71.1 s, 67.4 t, 55.0 q, 36.0 d, 25.2 t, 24.0 t, 13.5 q.

Methyl-3',4',5',6',7',8'-hexahydro-6'-methylspiro-[1,3-dioxolan-2,2'-(1'H)-napth-5'-oate (7a and 7b). To 22.0 g (0.1 mol) 6a/b in 20 ml tert.-butanol and 70 ml THF 1.7 l liquid ammonia and with stirring 10.0 g lithium (1.44 mol) were added in small portions. After 3 h the ammonia was evaporated and the residue was hydrolized by addition of methanol, water and 10% HCl. The crude, amorphous product (20.5 g) was directly used for the next step. To 20.5 g crude acids in 300 ml ether excess of CH_2N_2 was added. A small part was purified by TLC (Et_2O/petroleum ether, 2 : 1), colourless oil; Found: M^+ 222.127, $C_{13}H_{18}O_3$ requires 222.126. After evaporation to the residue in 200 ml ethyleneglycol and 50 ml CH_2Cl_2 60 ml trimethyl chlorosilane and after 36 h a $NaHCO_3$ solution were added. The reaction product was isolated by means of ether extraction. The crude product was purified by MCC with ether/petroleum ether mixtures affording 19.1 g (72%) of 7a and 7b which was directly used for the next step. A small part was separated by TLC (Et_2O/petroleum ether, 7 : 3). - ^{1}H NMR ($CDCl_3$): 7a: δ 2.32 and 2.09 (br d, H-4, J = 17 Hz), 1.88 (dddq, H-7, J = 12.5, 7, 3, 7), 2.91 (br d, H-8, J = 5.5), 0.94 (d, H-11, J = 7), 3.66 (s, OCH_3); 7b: δ 2.25 and 2.14 (br d, H-4, J = 17 Hz), 1.97 (m, H-7), 2.67 (br d, H-8, J = 8.5), 0.96 (d, H-11, J = 7), 3.69 (s, OCH_3).

Methyl-[5α',6α']-3',4',5',6',7',8'-hexahydro-6'-methyl-5'-(2-propenyl)-spiro-[1,3-dioxolane-2,2'(1'H)-naphth-5'-oate (8a). To a solution of LDA (from 8.4 g diisopropylamine in 120 ml THF and 33.3 ml 2.5 M n-butyl lithium in hexane) at -78° 18.8 g crude (0.069 mol) 7a/b in 30 ml THF was added. After 3 h stirring at -78° 10.1 g (0.083 mol) allyl bromide and after

18 h water were added. The crude product was directly used for the next step. A small part was purified by TLC (Et_2O/petroleum ether, 4 : 1). Colourless crystals, mp. 63° (Et_2O/petroleum ether). - Anal. calcd. for $C_{18}H_{26}O_4$: C, 70.54; H, 8.56; Found: C, 70.73; H, 8.52%.

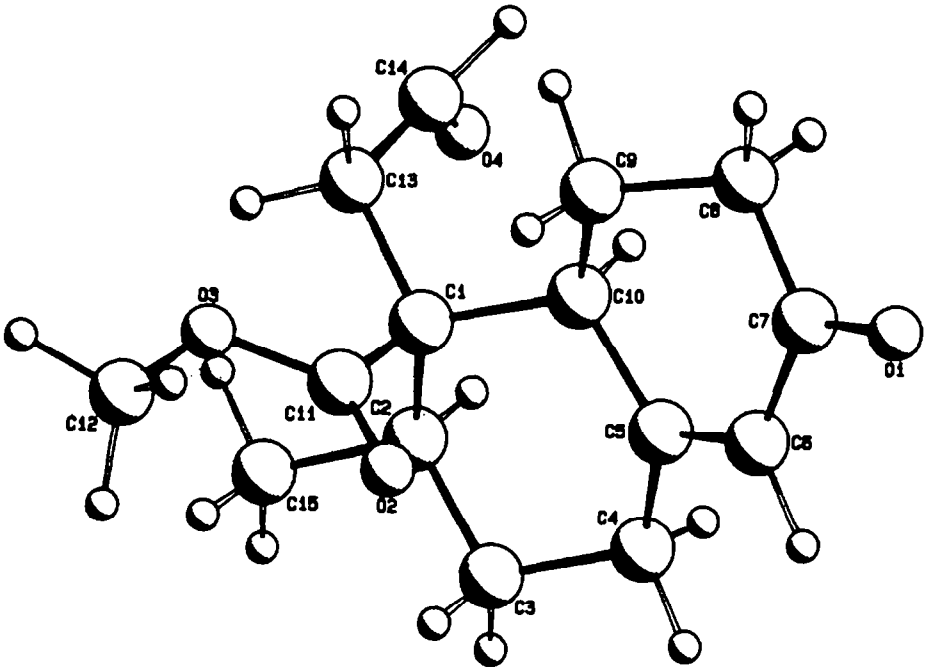
Methyl-[1α,2α,6x]-6-hydroxy-1,2,3,4,5,6,7,8-octahydro-1-(2-oxo-ethyl)-2,5,5-trimethyl-1-naphthoate (11a/b). To 40 g silica gel suspended in 400 ml CH_2Cl_2 10 ml 10% H_2SO_4 were added. After complete absorption of the water phase 19 g crude 8a in 100 ml CH_2Cl_2 was added. After 48 h stirring, filtration and evaporation the obtained residue was purified by MPC (Et_2O/petroleum ether) affording 10.0 g 8b (63%, based on 7). - ^1H NMR ($CDCl_3$): δ 2.59 - 2.01 (m, H-1, H-2 and H-4), 2.16 and 1.91 (m, H-6), 1.56 (dddd, H-7, J = 12, 5.5, 3.5, 3 Hz), 1.68 (dddd, H-7', J = 12, 12, 11.5, 4.5), 1.78 (ddq, H-8, J = 12, 7, 3), 2.59 (br dd, H-11, J = 14.5, 6.5), 2.53 (br dd, H-11', J = 14.5, 8), 5.44 (dddd, H-12, J = 17, 10, 8, 6.5), 5.07 (dd, H-13, J = 17, 1.5), 5.02 (br d, H-13', J = 10), 0.86 (d, H-14, J = 7), 1.22 (s, H-15), 1.12 (s, H-16), 3.67 (s, OCH_3); Found: M^+ 290.188 $C_{18}H_{26}O_3$ requires 290.188.

To 7.24 g 8b (27.4 mmol) in 20 ml tert.-butanol 6.2 g potassium-tert.-butoxide in 60 ml tert.-butanol was added. After 10 min 7.83 ml methyl iodide and after 30 min water was added. The reaction product was extracted with ether and the crude product was purifed by MPC affording 4.35 g (53%) of the dimethyl ketone which was reduced in 50 ml ethanol with 221 mg $NaBH_4$ affording a mixture of 10a and b (ca. 5 : 1); colourless oil; IR ν (cm^{-1}) ($CHCl_3$): 3600 (OH), 1720 (CO_2R); Found: M^+ 292.203 $C_{18}H_{28}O_3$ requires 292.204.

To 3.5 g 10a/b (12 mmol) in 30 ml THF, 10 ml tert.-butanol and 20 ml water 2.75 g N-methylmorpholine-N-oxide and 10 mg OsO_4 were added. After 3 d 2 g $NaHCO_3$ in 10 ml water was added. The crude diols were extracted with ether and stirred with 2.5 g $NaIO_4$ in 100 ml water. After 30 min the ether phase was evaporated and the reaction product was purified by MPC affording 1.74 g 11a (51%, based on 10a) and 0.34 g 11b (10%). 11a: Colourless oil; IR ν (cm^{-1}) ($CHCl_3$): 3600 (OH), 1725 (CO_2R); Found: M^+ 294.183 $C_{17}H_{26}O_4$ requires 294.183.

[1α'(S*),2α',6α']-5-(furanyl)-6'-hydroxy-3',4,4',5,5',6',7',8'-octahydro-2',5',5'-trimethylspiro[furan-3(2H),1'(2'H)-naphthalen]-2-one (14a). To a solution of 3-lithiumfuran (prepared from 3.87 g 3-bromofuran (26.4 mmol) and 26.4 mmol butyl lithium in 120 ml THF) at -65° 1.55 g (5.27 mmol) 11a in 30 ml THF was added. After 20 min 0.2 g potassium-tert.-butoxide in 10 ml tert.-butanol/THF (1 : 1) at -60° was added. When the temperature had raised to 20° water was added. Usual work-up afforded 1.65 g of a crude mixture of 14a/b (ca. 1 : 3) which was separated by TLC (Et_2O petroleum ether, 4 : 1). - 14a: Colourless crystals, mp. 183° (Et_2O). Anal. calcd. for $C_{20}H_{26}O_4$: C, 72.63; H, 7.93; found: C, 72.54; H, 8.19%. 14b: Colourless crystals, mp. 209° (Et_2O). Anal. calcd. for $C_{20}H_{26}O_4$: C, 72.63; H, 7.93; found: C, 72.43; H, 8.05%. Similarly 11b gave with 3-lithiumfuran a mixture of 14c and 14d (ca. 1 : 3) which could be separated by TLC (Et_2O/petroleum ether, 4 : 1). Found: M^+ 330.183 $C_{20}H_{26}O_4$ requires 330.183.

3α-Hydroxy-5β,10β-epoxychiliolide (15a) and its 12-epimer 15b. 1.65 g crude 14a/b in 150 ml CH_2Cl_2 was stirred for 16 h with 1.2 g m-chloroperbenzoic acid (80%). After shaking with Na_2CO_3-solution evaporation gave a crystalline mixture which was separated by MPC (Et_2O/petroleum ether mixtures) affording 204 mg 15a and 635 mg 15b.
15a: Colourless crystals, mp. 191.5° (Et_2O). Anal. calcd. for $C_{20}H_{26}O_5$: C, 69.33; H, 7.57; Found: C, 69.31; H, 7.58%.



Perspective view of the molecular structure of 12b

Table 3. Atomic positions

Atom	x	y	z	Ueq	atom	x	y	z	Ueq
C1	0.1496	0.3092	0.1330	0.0361	C11	0.2763	0.2362	0.1651	0.0357
C2	-0.0247	0.2998	0.1995	0.0471	C12	0.3673	0.1039	0.1153	0.0510
C3	0.0279	0.3037	0.3294	0.0518	C13	0.0917	0.3107	0.0005	0.0545
C4	0.1348	0.3806	0.3668	0.0474	C14	-0.0163	0.3844	-0.0465	0.0727
C5	0.2934	0.3998	0.3013	0.0346	C15	-0.1397	0.2229	0.1664	0.0850
C6	0.4517	0.4309	0.3546	0.0456	O1	0.7353	0.4980	0.3448	0.0855
C7	0.5925	0.4681	0.2937	0.0528	O2	0.3791	0.2306	0.2542	0.0528
C8	0.5472	0.4730	0.1661	0.0598	O3	0.2607	0.1775	0.0859	0.0456
C9	0.4352	0.3997	0.1168	0.0528	O4	-0.1493	0.4102	-0.0255	0.1645
C10	0.2568	0.3891	0.1723	0.0345					

Table 4. Bond lenghts

Atoms	distance	atoms	distance	atoms	distance
C1-C2	1.575 (3)	C4-C5	1.493 (3)	C9-C10	1.532 (3)
C1-C10	1.559 (3)	C5-C6	1.340 (3)	C11-O2	1.203 (3)
C1-C11	1.522 (3)	C5-C10	1.504 (3)	C11-O3	1.327 (3)
C1-C13	1.550 (3)	C6-C7	1.452 (4)	C12-O3	1.446 (3)
C2-C3	1.517 (4)	C7-C8	1.487 (4)	C13-C14	1.500 (4)
C2-C15	1.529 (4)	C7-O1	1.227 (3)	C14-O4	1.110 (5)
C3-C4	1.511 (4)	C8-C9	1.517 (4)		

Table 5. Bond angles

Atoms	angle	atoms	angle	atoms	angle
C10-C1-C2	109.8 (0.2)	C5-C4-C3	114.7 (0.2)	C5-C10-C1	113.5 (0.2)
C11-C1-C2	107.5 (0.2)	C6-C5-C4	120.7 (0.2)	C9-C10-C1	112.8 (0.2)
C11-C1-C10	108.8 (0.2)	C10-C5-C4	116.5 (0.2)	C9-C10-C5	111.3 (0.2)
C-13-C1-C2	111.3 (0.2)	C10-C5-C6	122.4 (0.2)	O3-C11-O2	122.4 (0.2)
C13-C1-C10	109.9 (0.2)	C7-C6-C5	123.4 (0.2)	C1-C11-O2	123.9 (0.2)
C13-C1-C11	109.5 (0.2)	C6-C7-O1	122.2 (0.3)	C1-C11-O3	113.6 (0.2)
C3-C2-C1	112.1 (0.2)	C8-C7-O1	121.8 (0.3)	C14-C13-C1	116.0 (0.2)
C15-C2-C1	113.7 (0.2)	C8-C7-C6	115.9 (0.2)	C13-C14-O4	130.7 (0.4)
C15-C2-C3	110.1 (0.3)	C9-C8-C7	112.0 (0.2)	C12-O3-C11	116.2 (0.2)
C4-C3-C2	112.0 (0.2)	C10-C9-C8	111.6 (0.2)		

15b: Colourless crystals, mp. 164° (Et_2O). Anal. calcd. for $C_{20}H_{26}O_5$: C, 69.33; H, 7.57; Found: C, 69.51; H, 7.56%.

Similarly 95 mg of a mixture of 14c/d (3 : 1) gave 32 mg 15c and 8 mg 15d. Found: M^+ 346.178 $C_{20}H_{26}O_5$ requires 346.178.

15c and 15d: IR$_\nu$ (cm^{-1}) (CCl_4): 3500 (OH hydrogen bonded). 16 mg 15a (0.046 mmol) in 5 ml CH_2Cl_2 was stirred for 3 h with 0.1 mmol pyridine chlorochromate on silica gel (10%). TLC (Et_2O/petroleum ether, 9 : 1) gave 12 mg 16 (75%); IR (cm^{-1}) (CCl_4): 1765 (γ-lactone), 1710 (C=O); CIMS: 345 (100%) $[M + 1]^+$ ($C_{20}H_{24}O_5$). 8 mg 16 (0.023 mmol) in 5 ml ethanol was reduced with 10 mg $NaBH_4$ affording 6 mg 15c, identical with the epoxide obtained from 14c (s.a.).

Methyl-[1α,2α,8aβ]-2-methyl-1,2,3,4,5,6,7,8a-octyhydro-6-oxo-1-(2-oxoethyl)-naphth-1-oate (12b). 1.47 g 9 (0.56 mmol) were heated in 20 ml methanol and 2 ml conc. HCl 4 h at 45°. After MPC (Et_2O/petroleum ether mixtures) 313 mg 9 (21%) and 310 mg 12a (21%), 1 g 12a (3.81 mmol) was degradated as 10a (s.a.) affording 520 mg 12b (36%); colourless crystals, mp. 94.5° (Et_2O). Found: M^+ 264.136 $C_{15}H_{20}O_4$ requires 264.136.

X-ray analysis: monoclin (p2/n), a = 7.255 Å, b = 16.334 Å, c = 11.682 Å, β = 97.52°, R = 0.0618, R_w = 0.0681, four molecules in the elementary cell. Atomic coordinates, bond lenghts and -angles are presented in Tables 3 - 5, lit.[9].

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9 Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein- Leopoldshafen 2, by quoting the names of the authors, and the journal citation.