ISSN 0018-019X
- Printed by Birkhäuser AG, Basel, Switzerland
Erscheint 9mal jährlich - Paraît 9 fois par an

37. The Reaction of Patchoulol with Lead Tetraacetate, a Regiospecific Fragmentation[1])

by **Alan F. Thomas** and **Michel Ozainne**

Firmenich SA, Research Laboratories, CH-1211 Geneva 8

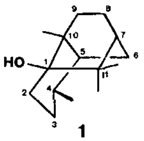
Dedicated to Prof. *E. Giovannini* on occasion of his 70th birthday

(20.XII.78)

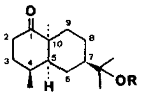
Summary

Patchoulol (**1**) forms 2,2,6,8-tetramethylbicyclo[5.3.1]undec-7-en-3-one (**5**) with lead tetraacetate. This ketone undergoes acid-catalyzed cyclization to 2,6,6,10-tetramethyltricyclo[5.3.1.$0^{1,5}$]undec-9-en-5-ol (**10**), and is reduced to 2 stereoisomeric alcohols with lithium aluminium hydride. One of these alcohols **8** is readily dehydrated with cyclization to 2,6,6,10-tetramethyltricyclo[5.3.1.$0^{1,5}$]undec-9-ene (**12**) and a double bond isomer **13**, longer treatment with acid resulting in a *Wagner-Meerwein* rearrangement to a mixture of two 1,3,7,7-tetramethyltricyclo[6.2.1.$0^{2,6}$]-undecenes (**19** and **20**), isomeric with *β*-patchoulene (**23**). The other alcohol **7** with *p*-toluenesulfonic acid forms the cyclic ether, 1,3,7,7-tetramethyl-11-oxatricyclo-[4.4.1.$1^{2,8}$]dodecane (**15**).

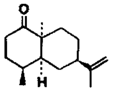
Patchoulol (**1**, *abeo*-guaiane numbering), the most important odour component of the oil from *Pogostemon cablin*[2]), is well known for its 'unprecedented rearrangements' [4]. In the course of structural work, the reactions of patchoulol with chromium trioxide and lead tetraacetate were examined [4] [5]. The latter reagent gives initially the hydroxylated decalone **2** (R = H) and its acetate **2** (R = $COCH_3$), which in turn dehydrate to **3** and **4** using longer reaction times [5], together with a further product to which no structure was assigned; this substance had no hydroxyl group (IR.) but led to an unsaturated alcohol after gas chromatography (GC.) [5]. The



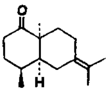
1



2



3



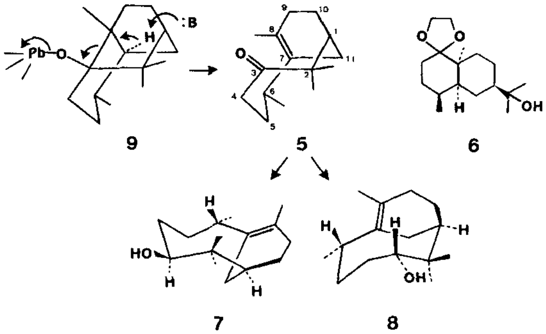
4

---

[1]) Preliminary communication, see [1]. In [1], the nomenclature and numbering of **12** are incorrect.

[2]) The statement from one laboratory that patchoulol is without odour [2] has never been confirmed elsewhere [3].

Scheme 1



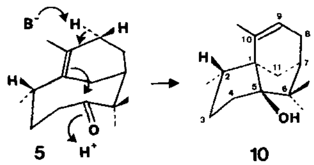
decalones **2** and **3** were also described more recently [6], together with a third product purporting to be an ether, but which we believe to be identical with *Gubler*'s unsaturated alcohol [5].

Treatment of patchoulol (**1**) with lead tetraacetate in the presence of calcium carbonate led to a mixture from which an almost pure ketone (IR.) was distilled in *ca.* 50% yield. Spectral data showed it to have 2 hydrogen atoms less than patchoulol (MS.), 2 gem-dimethyl groups, a secondary methyl group, and one methyl group on a tetrasubstituted double bond (^{1}H-NMR.). There was a strong presumption that this was 2,2,6-*exo*,8-tetramethylbicyclo[5.3.1]undec-7-en-3-one (**5**), this being supported by the ^{13}C-NMR. spectrum *(Table 1)*. The other products from the lead tetraacetate reaction were not extensively studied, but from the heavier fraction of the distillation, the hydroxyketone **2**, R = H, and its ethylene acetal (**6**, formed because excess lead tetraacetate had been destroyed with ethylene glycol) were characterized.

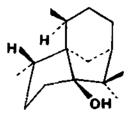
The ketone **5** was reduced with $LiAlH_4$ in ether to a mixture of 2 alcohols. These were separated by chromatography on silica gel; the alcohol eluted first was liquid, and subsequently was assigned the *endo*-configuration **7**. The more polar alcohol (**8**, *exo*) was crystalline, and distinctly more easily acetylated with acetic anhydride in pyridine than the *endo* isomer (**7**). Both the *exo*-alcohol (**8**) and its acetate were converted to hydrocarbons on attempted purification by GC. (see below), but the *endo*-alcohol **7** and its acetate were stable under these conditions.

Formation of a bicyclic unsaturated ketone from patchoulol (**1**) requires fission of a C(1)–C bond and loss of 2 protons. We feel that if a 'free' carbenium ion were involved, it would not lead to a single product (such a case is discussed below), and prefer a concerted reaction (**9**, *Scheme 1*), facilitated by the fact that the proton on C(5) is oriented *anti*-periplanar to the C(1)–O bond. Models imply that the ketone **5** can exist in 2 conformations, these approximating in shape to those of the 2 corresponding alcohols, **7** and **8**.

The bicyclo[5.3.1]undecene structures were supported by the reactions of the compounds with traces of acid. The ketone **5**, which we suppose is the substance to which *Gubler* did not assign a structure but which yielded an alcohol after GC. [5], is converted by passage through a GC. apparatus which is not scrupulously clean to an alcohol **10**, a reaction more conveniently carried out by treating the ketone **5** with *p*-toluenesulfonic acid in toluene. Attribution of structure **10** was based on the fact that this alcohol con-



5 **10**

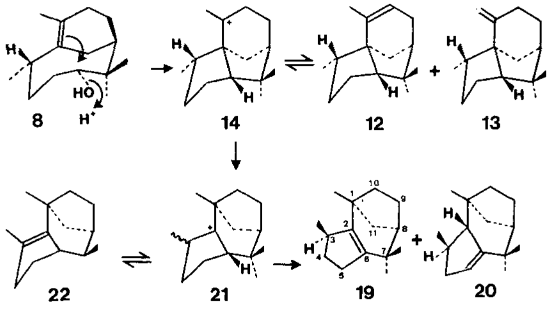


11

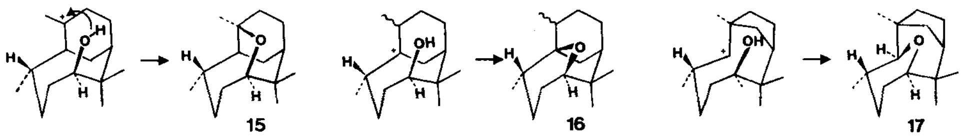
tains only one double bond (it was hydrogenated to the fully saturated alcohol **11**[3])), so, since it is isomeric with the ketone **5**, it must contain 3 rings. Such a cyclization has a precedent in the very ready cyclization of 1-formyl-5-methylenecyclooctane to a bicyclo[3.3.0]nonane [7], and is parallelled by the cyclization of the *exo*-alcohol **8** on acid-catalyzed dehydration (the *endo*-alcohol **7** undergoes a different reaction in acid which is discussed below). Very brief treatment of **8** with *p*-toluenesulfonic acid, or passage of **8** or its acetate through a GC. apparatus led to the formation of 2 tricyclic hydrocarbons (**12** und **13**) containing one double bond. This reaction presumably involves the participation of the double bond of **8**, probably *via* the carbenium ion **14** *(Scheme 2)*, and consequently establishes the configuration of the alcohols **7** and **8**, since participation of the double bond in dehydration of the *endo*-alcohol **7** would lead to impossibly strained fused cyclopentane rings.

The *endo*-alcohol **7** reacted much more slowly with *p*-toluenesulfonic acid than the *exo*-isomer **8**, but after 24 h was almost completely converted to an isomeric saturated ether. This cyclization could occur either before a *Wagner-Meerwein* rearrangement, yielding **15** or **16**, or after rearrangement, yielding **17** *(Scheme 3)*. The ^{1}H-NMR. spectrum clearly excluded **16** and **17** by indicating only one proton on a carbon atom adjacent to an oxygen atom (eliminating **17**), and only one CH_3CH group (**16** has two). The ^{13}C-NMR. spectrum is in accord, and is listed in *Table 1*, since this 11-oxatricyclo-[4.4.1.1^{2,8}]dodecane is an oxygen-bridged bicyclo[5.3.1]undecane.

Scheme 2



Scheme 3



---

[3] The methyl group on C(10) is placed *endo*, consistent with hydrogenation from the less hindered side of the double bond.

Table 1. *^{13}C-NMR. Signals of Various Bicyclo[5.3.1]undecanes*

Carbon atom number	1	2	3	4	5	6	7	8	9	10	11	Methyl groups			
Ketone **5**	46.6	50.4	217.3	38.1	23.1	33.6	133.9	133.0	29.8	25.2	34.1	17.8	18.1	24.6	26.0
endo-Alcohol **7**	41.8	42.2	79.4	32.3	23.5	32.1	130.3	139.5	30.2	24.5	28.8	17.5	19.5	28.2	(2)
exo-Alcohol **8**	43.6	42.0	74.4	32.1	24.0	32.6	129.5	135.6	30.9	24.5	34.7	17.4	19.0	22.2	25.9
3,8-Ether **15**[a])	40.6	42.4	82.3	32.8	29.9	29.3	46.7	76.2	33.7	31.9	36.5	22.6	22.7	23.8	26.8

[a]) Ether **15** is numbered *only in this table* as a bicyclo[5.3.1]undecane to facilitate comparison with the other compounds in the series.

Table 2. *^{1}H-NMR. Signals and Eu(fod)$_3$ Shifts of Bicyclo[5.3.1]undecanols*

	$H_3C-C(2)$		H−C(3)	$H_3C-C(6)$	H−C(6)	$H_3C-C(8)$	H(syn)−C(12)
	a	b					
endo-Alcohol **7**	0.94	1.03	3.39	0.99 ($J = 7$)	2.75	1.78	2.48 ($J = 13$)
Shift[a])	0.51	0.52	2.08	0.23	0.90	0.21	0.56
exo-Alcohol	0.90	1.02	3.59	0.99 ($J = 7.5$)	2.86	1.72	2.52 ($J = 13$)
Shift[a])	0.88	0.78	1.84	0.18	0.19	0.06	0.45

[a]) Shift (ppm) observed on addition of *ca.* 0.1 equiv. Eu(fod)$_3$.

The configurations of alcohols **7** and **8** are supported by the ^{13}C-NMR. spectra *(Table 1)*, where perhaps the most obvious difference lies between the chemical shifts of the signals for C(3), bearing the alcoholic function, and the bridge atom C(11). In the case of the *endo*-alcohol (**7**), C(11) is more shielded because of the quasi-parallel orientation of the bonds C(1)-C(11) and C(2)-C(3) compared with the isomer **8**, while in the latter, the carbon atom C(3) is more shielded because of the nearly parallel orientation of the H−C(3) bond with the C(1)-C(10) bond. To some extent these attributions are also supported by the ^{1}H-NMR. spectra *(Table 2)*. In particular, the displacements caused by the shift reagent, Eu(fod)$_3$, are much greater for protons situated on the same side of the 8-membered ring as the hydroxyl group (*i.e.* H−C(6) and $CH_3-C(8)$) in the *endo*-isomer **7** than in the *exo*-isomer **8**.

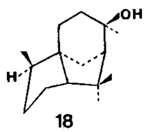
The structures of all the tricyclo[5.3.1.0^{1,5}]undecanes mentioned are supported by the ^{1}H-, and particularly the ^{13}C-NMR. spectra. The latter are listed in *Table 3*, in which we have included *Wenkert*'s figures for cedrol (**18**) [8], but interchanging his assignments of C(3) and C(10), and C(5) and C(7), to provide a better fit with our present results.

Hydrocarbons **12** and **13** are not stable under the conditions of their formation, and continued treatment of the *exo*-alcohol **8** with *p*-toluenesulfonic acid in toluene results in their disappearance, and formation of 2 new hydrocarbons **19** and **20** (*ca.* 1:5). Both

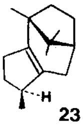
Table 3. *^{13}C-NMR. Signals of Various Tricyclo[5.3.1.0^{1,5}]undecanes*

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	Methyl groups			
12	59.0	36.8	31.0	25.1	63.0	44.4	47.0	34.1[a])	119.6	144.6	34.0[a])	15.1	19.1	27.8	29.1
13	61.6	37.6	31.6	24.5	57.5	44.0	47.8	35.3	29.2	156.1	38.5	14.7	26.0	26.1	100.9 (CH_2)
10	62.7	35.4	31.4[a])	31.0[a])	95.9	46.8	46.1	32.6	122.9	142.3	34.8	15.9	21.6	23.3	30.0
11	60.3	35.7	31.4	29.2	93.8	46.6	47.1	36.1	28.2	38.3	39.4	13.9	17.9	20.8	30.0
18	53.7	41.0	31.2	25.0	60.6	43.0	56.2	73.9	34.8	36.6	41.5	15.2	27.7	28.6	30.2

[a]) Assignments may be reversed



18



23

contain 3 CH_3-groups attached to quaternary carbon atoms and one CH_3CH-group (^1H-NMR.), so the simplest way to account for their formation is through a *Wagner-Meerwein* rearrangement of the ion **14** to **21** and subsequent deprotonation *(Scheme 2)*. Since deprotonation is reversible, and could involve **22** (although we were unable to detect this), we can no longer be certain about the configuration at the C(3)-atom. The 360-MHz-^1H-NMR. spectrum led us to prefer the *endo*-configuration for the methyl group, but some doubt remains.

In the ^1H-NMR. spectrum of **20**, the vinyl proton (C(5)) at 5.15 ppm is coupled with the protons at C(4) (H_{endo}–C(4) at 2.45 ppm and H_{exo}–C(4) at 1.82 ppm), with $J_{4endo,5} = 1.2$ Hz, $J_{4exo,5} = 1.0$ Hz, $J_{4exo,4endo} = 16$ Hz. The *exo* proton H_{exo}–C(4) is *cis* to the adjacent proton H–C(3) (at 1.99 ppm) by virtue of the larger coupling constant [9] ($J_{3,4exo} = 9$ Hz, $J_{3,4endo} = 7$ Hz) and H–C(2) is placed *trans* to H–C(3), also because of the coupling constant ($J_{2,3} = 7$ Hz). Proton H–C(2) (at 2.12 ppm) must be *endo*, since only in this position will it be possible to account for the long-range coupling observable with the highest field proton (0.94 ppm), which must be ascribed to H_{anti}–C(11) in accord with *Jefford & Ramey* [10]. Long-range homoallylic couplings between H–C(2) and H_{endo}–C(4) ($J_{2,4endo} = 3$ Hz) and between H–C(2) and H_{exo}–C(4) ($J_{2,4exo} =$ 1.5 Hz) are also visible.

The proton at lowest field in the 360-MHz-NMR. spectrum of **19** (at 2.71 ppm) must be H–C(3), and is coupled with H–C(4) ($J_{3,4exo} = 9$ Hz, $J_{3,4endo} = 7$ Hz, H_{exo}–C(4) at 1.93, H_{endo}–C(4) at 1.39 ppm). Only one long-range coupling is visible ($J_{3,5exo} = 2$ Hz) thus placing H_{exo}–C(5) at 2.22 ppm, and, since it is coupled with H_{endo}–C(5) ($J_{5exo,5endo} = 15$ Hz), H_{endo}–C(5) must be responsible for the signals at 2.06 ppm. The upfield position of H_{endo}–C(4) implies a distorted cyclopentene ring, bending down of the 'flap' C(3-4-5) causing H_{endo}–C(4) to be more 'axial-like', and more affected by the π-electrons of the double bond. Models suggest that the *endo* orientation of the H_3C–C(3) would be more stable, and possibly H_{exo}–C(5) would be at lower field than H_{endo}–C(5). This is generally the case for bicyclo[2.2.1]heptanes [11] and bicyclo[3.2.1]octanes [10], but it is uncertain whether this reasoning follows to the systems under consideration. An attempt to resolve the problem using β-patchoulene (**23**) as a model failed when we observed that both protons at C(3) were at 2.19 ppm. The ^{13}C-NMR. spectra of the 2 hydrocarbons **19** and **20** are in accord with the gross structure and with the spectrum of **23** (see experimental part), but did not assist us in assigning configuration.

We thank Miss *Danielle Schefer* for assistance with the experimental work, and Mr. *Walter Thommen* for measurement of the 360-MHz-^1H-NMR. and the ^{13}C-NMR. spectra.

Experimental Part

The ^1H- and ^{13}C-NMR. spectra were recorded in $CDCl_3$ on a *Bruker* HX-90 or a *Bruker* VH-360 instrument. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane, coupling constants J in Hz. Mass spectra were measured on an *Atlas* CH 4 mass spectrometer, using an inlet temperature of about 150° and electrons of 70 eV. Results are quoted as *m/e* (% most important fragment), and generally, the ten most important fragments are given. IR. spectra were obtained on a *Perkin-Elmer* type 125 spectrophotometer. Gas chromatography (GC.) was carried out on a *Carlo-Erba* type GT chromatograph with He as carrier gas.

Reaction of patchoulol (**1**) *with lead tetraacetate: 2,2,6,8-tetramethylbicyclo[5.3.1]undec-7-en-3-one* (**5**). A suspension of calcium carbonate (dried 2 h at 120°, 200 g) in benzene (3000 ml) was heated at reflux to remove water, then lead tetraacetate (450 g, freed from acetic acid by keeping at 10 Torr for 2 days over KOH pellets) was added and heating continued until all water was removed (1 h). The mixture was cooled to 40°, patchoulol (100 g, twice recrystallized from pentane) was added, then the mixture was heated at reflux for 3 h. Excess lead tetraacetate was decomposed by the cautious addition of 100 ml of ethylene glycol (initial vigorous reaction). After 15 min, the mixture was allowed to cool to RT. overnight, and the supernatant liquid was decanted, washed (saturated Na_2CO_3-solution, water), and concentrated. The residue was diluted with pentane, and the solution was filtered through 'Hiflo', concentrated and distilled, b.p. 84–95°/0.001 Torr, to yield 48.7 g of **5**, *ca.* 90% pure (by TLC.), and 49.8 g of residue, examination of which is described below. The ketone **5** was purified by distillation, b.p. 84–85°/0.001 Torr, $[\alpha]_D^{20} + 101°$ ($c = 12\%$, $CHCl_3$). - IR. (liquid): 1680, 1695 cm^{-1}, no OH band. - ^{1}H-NMR.: 1.01 (*s*, 3 H, $H_3C-C(2)$); 1.03 (*d*, $J = 7$, 3 H, $H_3C-C(6)$); 1.38 (*s*, 3 H, $H_3C-C(2)$); 1.44 (*d*, $J = 1$, 3 H, $H_3C-C(8)$); 2.5–3.1 (*m*, 4 H). - MS.: 220 (20, M^+). In view of the instability of the substance towards hot surfaces, the MS. is probably unreliable.

$C_{15}H_{24}O$ (220.34) Calc. C 81.76 H 10.98% Found C 81.87 H 10.82%

Part of the residue from the reaction (12 g) was filtered in $CHCl_3$ through 200 g of silica gel to remove inorganic material. A pale viscous oil (*ca.* 2 g) was obtained, b.p. 110–112°/0.01 Torr (bath temp.), which contained 2 products (GC., OV-17 column). The one with the shorter retention time was $4\beta,10\alpha$-dimethyl-11-hydroxy-eudesman-1-one (**2**, R = H), with spectra similar to those described [5]: ^{1}H-NMR.: 1.00 (*d*, $J = 6.5$, 3 H, $H_3C-C(4)$); 1.12, 1.16 and 1.23 (all *s*, 3 H). - MS.: 98 (100), 125 (88), 59 (79), 83 and 43 (69), 99 (57), 138 (55), 41 (50), 55 (43), 180 (42) ... 220 (14, $M^+ - 18$). - The other product with longer retention time was the ethylene acetal **6** of **2** (R = H), with ^{1}H-NMR.: 0.89 (*d*, $J = 6.5$, 3 H, $H_3C-C(4)$); 1.06 (*s*, 3 H, $H_3C-C(9)$); 1.17 (*s*, 6 H); 1.90 (*d*, *ca.* 1 Hz between peaks, 4 H, $O-CH_2CH_2-O$). - MS.: 99 (100), 86 (12), 163, 55 and 43 (8), 100 and 41 (6), 59 (4) ... 264 (3, $M^+ - 18$).

2,2,6,8-Tetramethylbicyclo[5.3.1]undec-7-en-3-ols **7** and **8**. A solution of the ketone **5** in abs. ether (50 ml) was added dropwise to $LiAlH_4$ (2.1 g) in abs. ether (200 ml) over 2 h. After 1 h under reflux, the mixture was cooled and the excess $LiAlH_4$ decomposed by the cautious addition of water. Filtration and concentration yielded 15.7 g of material which was purified by chromatography on silica gel (500 g) in a solvent mixture of polarity increasing from hexane/ether 8:2 to 7:3. The *endo*-isomer **7** was eluted first (4.7 g) and was purified by GC. on OV-17. The ^{1}H- and ^{13}C-NMR. spectra are in the theoretical part. - MS.: 41 (100), 93 (76), 119 and 81 (61), 107 (60), 55 (59), 105 and 43 (53), 121 and 91 (50) ... 189 (37), 204 (7), 207 (1), 222 (20, M^+).

$C_{15}H_{26}O$ (222.36) Calc. C 81.02 H 11.79% Found C 80.90 H 11.78%

The *acetate* was prepared by stirring the alcohol **7** (2 g) in acetic anhydride (2.26 g) and pyridine (2.3 ml) for 4 days at RT. followed by 10 h at 40°. The mixture was washed (hydrochloric acid 10%, $NaHCO_3$, water), dried, concentrated, and the residue distilled (bulb, bath temp. 160°/0.01 Torr). For analysis it was purified by GC. on SP 1000. - ^{1}H-NMR. (360 MHz): 0.87, 0.90, 1.65 and 2.00 (each *s*, 3 H); 0.94 (*d*, $J = 7$, 3 H); 4.72 ($d \times d$, $J = 4.5$ and 7, 1 H). - MS.: 43 (100), 119 (89), 93 (77), 105 (73), 41 (70), 161 (65), 204 (64), 121 (62), 107 (60), 147 (58) ... 220 (2), 264 (18.5, M^+).

$C_{17}H_{28}O_2$ (264.39) Calc. C 77.22 H 10.67% Found C 77.20 H 10.64%

The *exo*-alcohol **8** was eluted later and was purified by crystallization from hexane, m.p. 79–81°. The substance decomposed on GC. - NMR. spectra are in the theoretical part. - MS.: 41 (100), 81 (92), 93 (83), 109 (75), 55 (70), 161 and 43 (67), 107 and 105 (66) ... 189 (36), 204 (27), 207 (22), 222 (32, M^+).

$C_{15}H_{26}O$ (222.36) Calc. C 81.02 H 11.79% Found C 81.04 H 11.65%

The acetate was prepared by dissolving the alcohol **8** (1 g) in acetic anhydride (1.13 g) and pyridine (1.12 ml) at RT. for 5 h. Workup as for the acetate of **7** yielded practically pure **8**-acetate, which was purified by bulb distillation (bath temp. 150°/0.01 Torr). GC.: decomposes this acetate. - ^{1}H-NMR. (360 MHz): 0.69, 1.01, 1.70 and 1.90 (each *s*, 3 H); 0.89 (*d*, $J=7$, 3 H); 2.80 (*qa*, $J=7$, 1H); 4.81 ($d\times d$, $J=3$ and 7, 1H). - The MS. is probably unreliable because of decomposition on hot surfaces.

$C_{17}H_{28}O_2$ (264.39) Calc. C 77.22 H 10.67% Found C 77.27 H 10.67%

2-exo,*6,6,10-Tetramethyltricyclo[5.3.1.0^{1,5}]undec-9-ene* (**12**) and 2-exo,*6,6-trimethyl-10-methylenetricyclo[5.3.1.0^{1,5}]undecane* (**13**). A solution of the alcohol **8** (0.5 g) in toluene (50 ml) containing *p*-toluenesulfonic acid (0.001 g) was heated under reflux. After 10 min, the alcohol **8** had disappeared, and the solution was cooled, washed (Na_2CO_3, water), and concentrated. The products were purified by GC. on OV-17, the hydrocarbon **12** having a shorter retention time, and the following spectra. - ^{1}H-NMR.: 0.89 (*d*, $J=6.5$, 3H, $H_3C-C(2)$); 0.96 and 1.06 (each *s*, 3H); 1.68 (*d*, $J=1.5$, 3H, $H_3C-C(10)$); 2.10-2.15 (*m*, 2 H); 5.12 (br. *s*, $w\frac{1}{2}$ *ca.* 8 Hz, H-C(9)). - MS.: 124 (100), 81 (51), 119, 93 and 80 (43), 41 (37), 123 (34), 105 (32), 107 and 91 (27), 204 (25, M^+).

$C_{15}H_{24}$ (204.34) Calc. C 88.16 H 11.84% Found C 88.25 H 11.73%

The second hydrocarbon (**13**) had the following spectra. - ^{1}H-NMR.: 0.96 (*d*, $J=6.5$, 3 H, $H_3C-C(2)$); 0.96 and 1.07 (each *s*, 3 H); 2.20-2.40 (*m*, 2 H); 4.53 and 4.55 (each *s*, 1H). - MS.: 189 (100), 41 (68), 161 (67), 204 (65, M^+), 123 and 81 (57), 93 (50), 91 (48), 105 and 107 (43).

$C_{15}H_{24}$ (204.34) Calc. C 88.16 H 11.84% Found C 88.00 H 11.77%

The same substances were obtained (in about the same ratio, **12**:**13** = 4:1) with identical retention times and spectra, when **8** was injected into a GC. apparatus (evaporator 220°, OV-17 column).

1,3,7,7-Tetramethyltricyclo[6.2.1.0^{2,6}]undec-2(6)-ene (**19**) and *1,3,7,7-tetramethyltricyclo[6.2.1.0^{2,6}]undec-5-ene* (**20**). The experiment was carried out as described for **12** and **13** (above), but using 0.05 g of *p*-toluenesulfonic acid, and heating under reflux for 24 h. GC. on OV-17 then yielded 2 products in a ratio of 1:5. The hydrocarbon of shorter retention time was **19**, with the following spectra. - ^{1}H-NMR. (360 MHz): 0.93, 1.00 and 1.15 (each *s*, 3 H); 0.99 (*d*, $J=7$, 3 H); see theoretical part for further details. - ^{13}C-NMR.: 21.4, 21.6, 24.9 and 27.9 (CH_3), 25.8 (C(5)), 28.6 (C(9)), 31.5 (C(10)), 37.6 (C(7)), 39.9 (C(3)), 40.8 (C(11)), 40.9 (C(1)), 43.6 (C(4)), 47.4 (C(8)), 138.3 (C(6)), 145.5 (C(2)). - MS.: 161 (100), 119 (85), 189 (79), 204 (47, M^+), 105 (26), 133 (24), 41, 93 and 147 (22), 91 and 135 (19).

Hydrocarbon **20** had the following spectra: ^{1}H-NMR. (360 MHz): 1.02 (*s*, 9 H); 1.08 (*d*, $J=6.5$, $H_3C-C(3)$); see also theoretical part. - ^{13}C-NMR.: 23.1, 24.5, 26.0 and 27.4 (CH_3), 27.1 (C(9)), 30.8 (C(10)), 33.8 (C(3)), 37.4 (C(7)), 40.8 (C(4)), 43.5 (C(11)), 44.7 (C(1)), 48.5 (C(8)), 62.1 (C(2)), 119.7 (C(5)), 151.4 (C(6)). - MS.: 81 (100), 124 (87), 123 (70), 80 (38), 41 (17), 107 and 122 (15), 204 (14, M^+), 91 (13). The microanalysis was carried out on the mixture of **19** and **20**.

$C_{15}H_{24}$ (204.34) Calc. C 88.16 H 11.84% Found C 87.60 H 11.86%

1,3,7,7-Tetramethyl-11-oxatricyclo [4.4.1.1^{2,8}]dodecane (**15**). A solution of alcohol **7** (0.5 g) in toluene (50 ml) containing *p*-toluenesulfonic acid (0.001 g) was heated under reflux for 6 h, when there was no more starting material remaining. The solution was washed (Na_2CO_3, water) and concentrated, and the product was purified by chromatography on silica gel. For analysis, the ether **17** was purified by GC. (OV-17). - ^{1}H-NMR. (360 MHz): 0.91 (*d*, $J=6.5$, H_3C-CH); 0.98, 1.09 and 1.23 (each *s*, 3 H); 2.18 (*m*, $J=5$, 6.5 and 11); 3.63 (*t*, $J=4$). - ^{13}C-NMR.: see *Table 1*. - MS.: 82 (100), 122 (39), 41, 43 and 81 (35), 137 (30), 55 and 95 (29) ... 204 (9), 207 (2), 222 (18, M^+).

$C_{15}H_{26}O$ (222.36) Calc. C 81.02 H 11.79% Found C 81.17 H 11.73%

2-exo,*6,6,10-Tetramethyltricyclo[5.3.1.0^{1,5}]undec-9-en-5*endo-*ol* (**10**). A solution of the ketone **5** (2 g) in toluene (30 ml) and *p*-toluenesulfonic acid (0.1 g) was heated under reflux for 2 h. After washing ($NaHCO_3$, water), the toluene was evaporated and the residue distilled (bulb) to yield 1.7 g of material (bath temp. 75-100°/0.01 Torr). For analysis, this was purified by GC. on OV-17. $[\alpha]_D^{20}+151°$ ($c=11\%$, $CHCl_3$). - IR. (CCl_4): 3560 cm^{-1}, no C=O band. - ^{1}H-NMR. [5] [6]: 0.94 (*d*, $J=6.5$, 3 H, $H_3C-C(2)$); 0.98 and 1.04 (each *s*, 3 H, $H_3C-C(6)$); 1.72 (*d*, $J=1.5$, 3 H, $H_3C-C(10)$); 5.42 (br., 1H, H-C(9)). - MS.: 41 (100), 159 (89), 93 and 43 (80), 121 (68), 55 (64), 138 and 107 (61), 91 (60) ... 220 (43, M^+).

$C_{15}H_{24}O$ (220.34) Calc. C 81.76 H 10.98% Found C 81.55 H 10.96%

The same substance **10** was also isolated on injecting crude ketone **5** into a GC. apparatus (evaporator 220°, OV-17 column). In this case a second peak (*ca.* 10% of the total) was identified as the *cis*-eudesman-1-one (**4**) (*cf.* [5] [6]). - ^{1}H-NMR.: 1.03 (*d*, $J = 6.5$, 3 H, $H_3C-C(4)$); 1.22 (*s*, 3 H, $H_3C-C(9)$); 1.64 (*s*, 6 H, $H_3C-C=$); 2.1-2.9 (*m*, 6 H). - MS.: 125 (100), 96 (33), 43 (23), 41 (19), 107 (16), 55 (13), 220 (12, M^+), 81 (11).

*2-*exo*,6,6,10-*endo*-Tetramethyltricyclo[5.3.1.0^{1,5}]undecan-3-*endo*-ol* (**11**). A solution of **12** (0.5 g) in ethanol (13 ml) was shaken in H_2 with 10% Rh/C (0.05 g). After 24 h, the theoretical amount of H_2 was absorbed, and the mixture was filtered, concentrated, and purified by GC. (OV-17 column) $[\alpha]_D^{20} + 14.3°$ ($c = 10\%$, $CHCl_3$). - IR.: 3625 cm^{-1}. - ^{1}H-NMR.: 0.84 (*d*, $J = 6.5$, 3 H, $H_3C-C(2)$); 1.00 and 1.01 (each *s*) superimposed on *ca.* 1.07 (*d*) (together 9 H); 2.0-2.4 (*m.*, *ca.* 2 H); no vinyl H. - MS.: 125 (100), 111 (98), 41 (79), 55 (63), 110 and 81 (57), 43 (53), 123 (50), 82 (49), 67 (46) ... 222 (23, M^+).

*1,5-*exo*,11,11-Tetramethyltricyclo[6.2.1.0^{2,6}]undec-2(6)-ene* (β-patchoulene) (**23**) was prepared by dehydrating patchoulol (**1**) with iodine [12]. It had the following spectra. - ^{1}H-NMR. (360 MHz): 0.88 (*s*, 6 H); 0.90 (*s*, 3 H); 0.93 (*d*, $J = 6.5$, $H_3C-C(5)$); 1.30 (*m*, $H_{exo}-C(4)$); 2.03 (*m*, $H_{endo}-C(4)$); 2.19 (*m*, 2 H, $2\,H-C(3)$); 2.30 (br. *d*, $J = 3$ and 17, $H_{exo}-C(7)$); 2.45 (*m*, $J_{4exo,5endo} = 6$, $J_{4endo,5endo} = 8$, $H_{endo}-C(5)$). - ^{13}C-NMR.: 15.1, 18.9, 19.2, 23.5 (CH_3), 29.2, 30.5 (C(3) and C(9)), 32.7, 34.1 (C(7) and C(10)), 40.6 (C(4)), 42.6 (C(5)), 43.2 (C(1)), 44.8 (C(8)), 45.1 (C(11)), 134.4 (C(6)), 142.7 (C(2)).

REFERENCES

[1] *A.F. Thomas & M. Ozainne*, J. chem. Soc. Chem. Commun. *1977*, 120 and 392.

[2] *P. Teisseire, P. Maupetit & B. Corbier*, Recherches *19*, 8 (1974).

[3] *D. Kastner*, Riechstoffe, Aromen, Kosmetika *1977*, 79.

[4] *M. Dobler, J.D. Dunitz, B. Gubler, H.P. Weber, G. Büchi & J. Padilla O.*, Proc. chem. Soc. *1963*, 383.

[5] *B. Gubler*, Promotionsarbeit, ETH, Zürich 1965.

[6] *G. Mehta & B.P. Singh*, Tetrahedron Letters *1975*, 4495.

[7] *S.H. Graham & D.A. Jonas*, Chem. Commun. *1968*, 1091.

[8] *E. Wenkert, B.L. Gašić, H.E. Gottlieb, E.W. Hagaman, F.M. Schell & P.M. Wovkulich*, in Topics in carbon-13 NMR. spectroscopy, vol. 2 (ed. G.C. Levy), Wiley, New York 1976, p. 81. See also *L.F. Johnson & W.C. Jankowski*, 'Carbon-13 NMR. spectra', Wiley, New York 1972, Spectrum 466.

[9] *J.B. Lambert, J.J. Papay, S.A. Khan, K.A. Kappauf & E.S. Magyar*, J. Amer. chem. Soc. *96*, 6112 (1974).

[10] *C.W. Jefford & K.C. Ramey*, Tetrahedron *24*, 2927 (1968).

[11] *J.L. Marshall & S.R. Walter*, J. Amer. chem. Soc. *96*, 6358 (1974).

[12] *G. Büchi, W.D. MacLeod & J. Padilla O.*, J. Amer. chem. Soc. *84*, 4438 (1964).