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272. New Sesquiterpene Alcohols from *Galbanum* Resin; the Occurrence of C(10)-epi-Sesquiterpenoids

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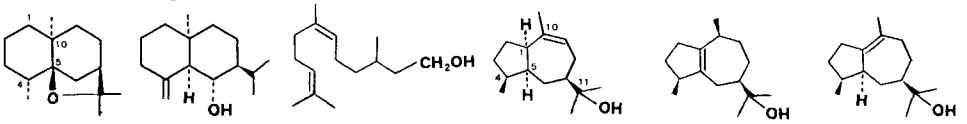
(4.X.78)

Summary

(+)-β-Eudesmol (**7**), (+)-10-epi-elemol (**8**), (−)-(Z)-dihydrofarnesol (**3**), and an alcohol believed to be a guai-9-en-11-ol (**4**) have been isolated from *Galbanum* resin. Together with (−)-β-dihydroagarofuran (**1**) and epi-ligulyl oxide (**13**) (reported naturally occurring for the first time), 10-epi-elemol (**8**) and 10-epi-junenol (**2**) involve the enantiomeric stereochemistry at C(10) compared with β-eudesmol **7**, and guaiol **5**, the major sesquiterpene alcohol of *Galbanum*.

We have already reported the occurrence of (−)-β-dihydroagarofuran[1]) (**1**) [1] and (+)-10-epi-junenol (**2**) [2] in the resin from *Ferula* species *(Galbanum),* and we now add two further C(10)-epi-sesquiterpenoids and the alcohols (−)-(*Z*)-dihydrofarnesol **3** and guai-9-en-11-ol **4** to this list.

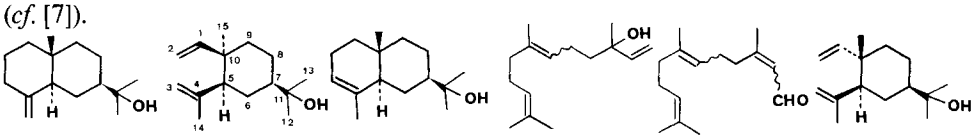


1 **2** **3** **4** **5** **6**

Galbanum resin was worked up successively by solvent extraction and distillation. From the heavier fractions of the distillations (see exper. part), a more polar fraction was isolated by chromatography on silica gel. Preparative gas chromatography (GC.) was used to separate most of the major sesquiterpene alcohol, guaiol (**5**) [3], and the remainder of the fraction was then chromatographed on silica gel impregnated with silver nitrate. A complex mixture of sesquiterpene alcohols was eluted from this column, from which the following were identified: bulnesol (**6**), known to occur in *Galbanum* oil [3], (+)-β-eudesmol (**7**), (−)-(*Z*)-dihydrofarnesol (**3**), 10-epi-elemol[2]) (**8**), and an alcohol to which we tentatively ascribe formula **4** (guai-9-en-11-ol).

α-Eudesmol **9**, in admixture with guaiol (**5**) and bulnesol (**6**) was already known to occur in *Galbanum* oil [3][3]), but we did not find **9** in this fraction.

(−)-(*Z*)-Dihydrofarnesol (**3**) was identified by comparison with (±)-(*Z*)-dihydrofarnesol prepared from the nerolidols (**10**). These are readily separated by preparative GC. or distillation, and were separately oxidatively rearranged (CrO_3) to the corresponding farnesals (**11**), which were then reduced with sodium in liquid ammonia. Direct reduction of a commercial mixture of farnesols over a Pt/C catalyst yielded a mixture from which the dihydrofarnesols can be purified by preparative GC. The isomers are readily distinguished by their GC. retention times (especially on *Carbowax*, (*Z*) having a shorter one than (*E*)), and their ^{1}H-NMR. spectra (*cf.* [7]).



7 **8** **9** **10** **11** **12**

Although dihydrofarnesols were described in 1924 [8], it was only in 1972 that one was suspected as a natural product, having been formed by enzymatic reduction of farnesols by rose petals [9]. One has also been found in *Camposcolia ciliata* female wasps [10], and one is the main marker secretion of *Bombus jonellus (Hym. Apidae)* males [11].

(+)-10-Epi-elemol (**8**) possesses a somewhat similar ^{1}H-NMR. spectrum to

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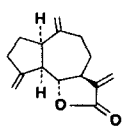
[1]) The rotation was not given in [1]: see experimental part of this communication.

[2]) The numbering of the elemane skeleton (*cf.* [4]) conforms to that of the eudesmanes and guaianes.

[3]) The original name 'galbanol' of this mixture [5], despite a recommendation that it should be deleted from the literature [3] has, nevertheless recently been (incorrectly) resuscitated [6].

that of (+)-elemol **12**, and an almost identical mass spectrum. The two compounds are distinguishable by their m.p., optical rotation, and the signals of the vinyl group protons, as well as by the shifts induced in the ^{1}H-NMR. spectrum by Eu(fod)$_3$. The only significantly different shifts between **8** and **12** are those induced in the angular methyl group, C(15) (shift/equiv. Eu(fod)$_3$: 0.10 for **8** and 0.22 for elemol **12**) and the protons of the vinyl group (C(1)–H shift is 0.26 for **8** and 0.12 for **12**). Our spectra are identical with those of *Kodama et al.* [12], who have synthesized the racemate of **8**[4]), and the considerably higher m.p. (69°) we find for the natural product must be because it is a single optical isomer.

The mass spectrum of the alcohol to which we attribute formula **4** is very similar to that of bulnesol (**6**), and the presence of an important fragment at *m/e* 59 implies the presence of the propan-2-ol group. The 90 MHz ^{1}H-NMR. spectrum *(Fig.)* shows the presence of a secondary methyl group and a methyl group attached to a double bond carrying a proton on its other end. The 360 MHz ^{1}H-NMR. spectrum enabled the coupling constants of this proton with two other protons to be measured, and the values (4.2 and 6.3 Hz) were greater than would be expected if the double bond were in a 5-membered ring (*cf.* [13]), so we place it at C(9) in a guaiane skeleton. The two protons with which the vinyl proton is coupled are situated at *ca.* 2.17 and 1.90 ppm. Another saturated proton is at 2.30, and this is coupled (*ca.* 9 Hz) with one at 2.53 ppm, these two protons are assigned to the bridgehead carbon atoms C(5) and C(1) respectively. If this is correct, the coupling constant $J_{1,5}$, is about the same as that between the corresponding protons in the *cis*-fused dihydrocostus lactone **13**[5]) [14]. The *Table* lists the ^{13}C-NMR. signals we have found for the new substance, presumed to be **4**, guaiol (**5**) and bulnesol (**6**). The similarity of the methyl group signals of bulnesol and the new compound is striking, and implies the same configuration about C(4) and C(5), if we may base the reasoning on the values for the 1,2-dimethylcyclopentanes in which the methyl groups of the *cis*-isomer have their ^{13}C-NMR. signal at 14.9 ppm, the *trans*-isomer having the corresponding signal at 18.5 ppm [15]. The attributions listed are tentative, but it should be noted that the figure given for C(1) of compound **4** fits a *cis* ring junction better than a *trans* one, for which we might expect a somewhat higher value. Thus, to the basic figure for the bridgehead carbon atoms of *cis* and *trans*-bicyclo[5.3.0]decanes (**14** and **15**, 42.0 and 46.5, respectively [16]), must be added a contribution for the methyl group at C(4). The effect of this on C(1) must be very small; again based on *Roberts et al.* [15] it might be −1.6 or +0.2, depending on the configuration, while the double bond will involve a further small



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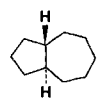

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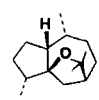

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[4]) We are grateful to Dr. *Kodama* and Professor *Itô* for discussion and the spectra of their (±)-10-epi-elemol.

[5]) We thank Dr. *Bruno Maurer* for this information prior to publication.

change. The chemical shifts of the figure for C(5), however, should be increased by *ca.* 2.8 for a *cis* C(4)-methyl or 7.9 for a *trans* C(4)-methyl group [15]. Using the *cis*-fused model (**14**) [16], the actual changes observed are −1.5 at C(1) and +5.2 at C(5). Furthermore, the increase in the value of the C(5)-resonance between bulnesol (**6**) and **4** is similar to that between C(2) of methylenecyclopentane [17] and methylcyclopentane [15].

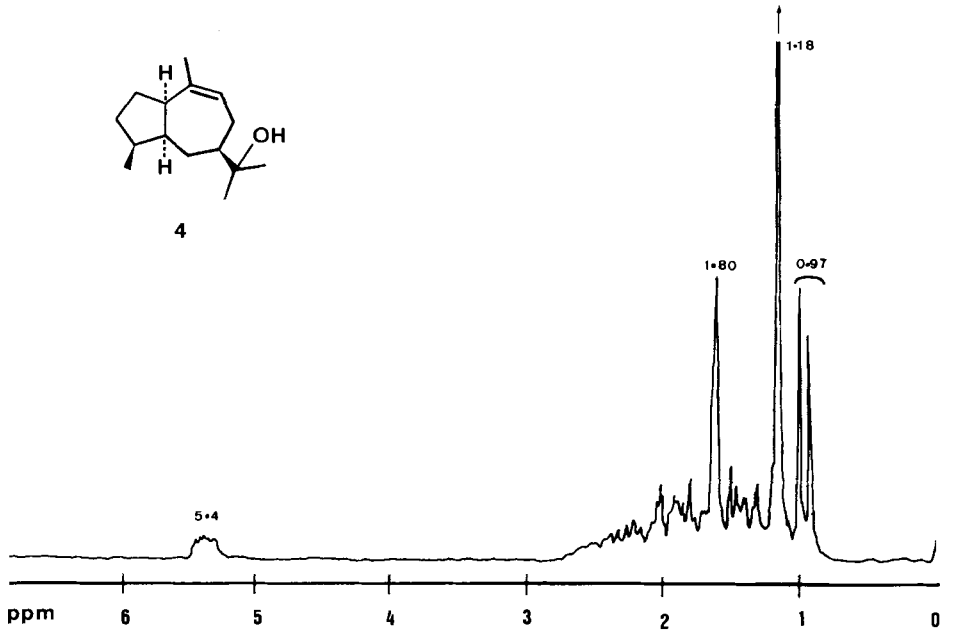
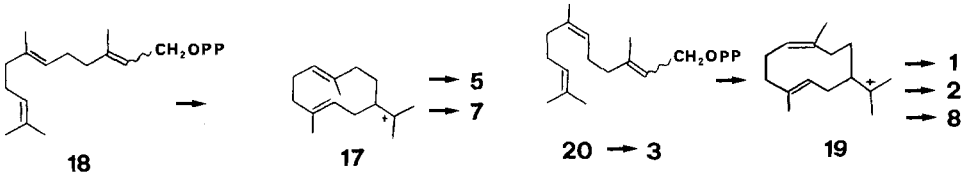


Figure. ^1H-*NMR. Spectrum of Compound* **4**

Table. ^{13}C-*NMR. Spectra of Guaiol Isomers*

Multiplicity	**4**		**5**		**6**	
qa	16.1	C(15)	19.8	C(14 or 15)	15.3	C(15)
	23.9	C(14)	19.9	C(15 or 14)	22.3	C(14)
	26.9	C(12 and 13)	25.9	C(12,13)	27.1	C(12,13)
			27.3		27.2	
t	24.9	C(3)	27.3	C(3)	27.8	C(3)
	28.6	C(2)	27.8	C(2)	28.8	C(2)
	28.6	C(6,8)	31.0		30.3	
	29.1		33.7		33.0	
			35.3		34.9	
d	39.2	C(4)	33.7	C(4)	39.0	C(4)
	40.5	C(1)	46.3	C(10)	46.3	C(5)
	47.2	C(5)	49.5	C(7)	54.1	C(7)
	50.5	C(7)				
	122.0	C(9)				
s	74.1	C(11)	73.4	C(11)	74.0	C(11)
	139.2	C(10)	138.9	C(1,5)	125.3	C(10)
			139.9		139.9	C(1)

From a lower boiling, less polar fraction of *Galbanum* resin, we isolated (−)-β-dihydroagarofuran (**1**) [1] and epi-ligulyl oxide (**16**) [18][6]) (for details see exper. part), both of which are 10-epi-compounds like 10-epi-junenol (**2**) and 10-epi-elemol (**8**). Current biogenetic theory suggests that the 'normal' series (elemol (**12**), guaiol (**5**), *etc.*) is derived by cyclization of an (*E, E*)-germacrane derivative (*e.g.* **17**) which, in turn, arises from (*E, E*)-farnesyl pyrophosphate (**18**) [19]. In order to arrive at 10-epi-compounds of the type we have found in *Ferula* species, a (*Z, E*)-germacrane derivative **19** is required, *i.e.* a (2*E*,6*Z*)-farnesyl pyrophosphate (**20**). Biosynthetic type syntheses of this kind have been carried out by *Itô* [12] [20]. It is noteworthy that we have found the related (*Z*)-dihydrofarnesol (**3**) in the same plant, and, since guaiol (**5**) and β-eudesmol (**7**) co-occur, the sesquiterpenes of this species presumably arise from both farnesol precursors.



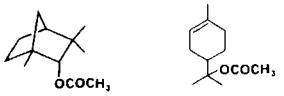
18 **17** **20** → **3** **19**

Added in proof: A recent paper reports the presence of other sesquiterpenoids and some macrolides in *Galbanum* resin [23].

Experimental Part

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

Extraction of *Galbanum* resin. The extraction mainly followed lines similar to those described [2]. Commercial *galbanum* resin (14.7 kg) was stirred with pentane (*ca.* 20 l). The lower layer was diluted with methanol (70% aqueous, *ca.* 10 l), and re-extracted with pentane (10 l). The combined pentane extracts were concentrated to yield *ca.* 5 kg of material which was stripped of the lighter fraction (mostly monoterpenoid hydrocarbons) by distillation up to b.p. 50°/10 Torr. The less volatile residue was distilled on a *Leybold-Hereus* thin film distillation apparatus to yield 1.3 kg of material from two passages: one at 100°/0.05 Torr, and a second at 170°/0.01 Torr. This crude extract contained the majority of the sesquiterpenoid material, and was distilled (*Vigreux* column) to remove fraction **A** with b.p. 100/0.001 Torr, and leaving a residue, **B**. From 360 g of fraction **A**, 21.8 g had b.p. 49–70°/0.001 Torr. Chromatography of this on silica gel in hexane containing increasing amounts of ether yielded first, a fraction (10.6 g) mostly containing hydrocarbons, followed by 3.7 g of a mixture eluted with hexane/ether 95:5. This mixture consisted mainly of fenchyl acetate **21** and α-terpinyl acetate **22**, the proportion of the latter increasing with increasing polarity of the solvent. These two substances accounted for *ca.* 70% of the fraction, but GC. (*Carbowax* column) enabled the following substances to be identified.



21 **22**

[6]) We are most grateful to Dr. *G. Lukacs*, Gif-sur-Yvette, for giving us the ^{13}C-NMR. spectrum of authentic epi-ligulyl oxide (**16**).

β-Dihydroagarofuran, $[\alpha]_D^{20} - 78°$ ($c = 1\%$, $CHCl_3$). – ^{1}H-NMR. [1] showed the presence of a trace of α-dihydroagarofuran. – MS.: 207 (100), 137 (76), 109 and 41 (50), 43 (46), 55 (41), 69 (37), 95 and 81 (30), 189 and 149 (29) ... 222 (10, M^+).

Epi-ligulyl oxide [18]. – ^{1}H-NMR.: 0.85 (*d*, $J = 6$, 3 H); 0.90 (*d*, $J = 6.5$, 3 H); 1.20 and 1.32 (each *s*, 3 H). – ^{13}C-NMR.: 13.8 (*qa*, CH_3–C(4)); 18.7 (*t*, C(2)); 21.5 (*qa*, CH_3–C(10)); 25.7 (*qa*, CH_3–C(11)); 25.7 and 25.9 (each *t*, C(8 and 9)); 27.5 (2*t*, C(3) and C(6)); 31.3 (*d*, C(10)); 32.3 (*qa*, CH_3–C(11)); 40.1 (*d*, C(4)); 44.1 (*d*, C(7)); 51.9 (*d*, C(1)); 83.1 (*s*, C(11)); 92.8 (*s*, C(5)). – MS.: 207 (100), 137 (72), 189 (64), 109 (57), 81 (56), 55 and 41 (55), 43 (47), 149 (46), 95 (45) ... 222 (13, M^+).

Examination of residue B. – This material was first filtered through silica gel in hexane to remove hydrocarbons and other less polar substances. Elution with hexane/methanol 95:5 yielded a fraction (35 g) from which guaiol (**6**) was separated by preparative GC. (*Apiezon* L column). The general discharge from this separation (16.3 g) was chromatographed on silica gel impregnated with $AgNO_3$, eluting with hexane containing increasing amounts of ether. From a fraction (1.7 g) eluted with ether (100%), the following were purified by GC. (*SP* 1000 column).

Bulnesol (**6**). Identical (NMR., MS., retention time) with authentic material.

β-Eudesmol (**7**). $[\alpha]_D^{20} + 54°$ ($c = 5.4\%$ in $CHCl_3$). – ^{1}H-NMR.: 4.45 and 4.72 (each *s*, 1 H), with no trace of a signal at 5.32 corresponding to α-eudesmol[7]).

(*Z*)-*Dihydrofarnesol* (**3**). $[\alpha]_D^{20} - 4°$ ($c = 1.03\%$, $CHCl_3$). – ^{1}H-NMR.: 0.91 (*d*, $J = 6$, 3 H); 1.62 (, 3 H); 1.70 (2 maxima, 1 H apart, 6 H in all); 2.0–2.1 (apparent *d*, *ca.* 6 H); 3.68 (*t*, $J = 6$, 2 H); 5.12 (*t*, $J = 6$, 2 H). – MS.: 69 (100), 41 (57), 81 (45), 95 (28), 123 and 55 (24), 43 (19), 67 (18), 181 (17) ... 224 (1, M^+).

10-Epi-elemol (**8**). M.p. 68–69.5°, $[\alpha]_D^{20} + 34°$ ($c = 1.2\%$, $CHCl_3$). – ^{1}H-NMR.: 1.03 (*s*, 3 H); 1.21 (*s*, 6 H); 1.70 (br. *s*, 3 H); 2.00 (*d* × *d*, $J = 5$ and 10, 1 H, H–C(5)); 4.65 and 4.79 (each *s*, 1 H); 5.00 (*d*, $J = 18$, 1 H); 5.05 (*d*, $J = 11$, 1 H); 6.30 (*d* × *d*, $J = 11$ and 18, 1 H). – MS.: 59 (100), 93 (78), 161 (77), 107 and 81 (49), 189 (47), 121 (42), 43 (40), 41 (39), 204 (37, $M^+ - 18$), M^+ (0).

cis-*Guai-9-en-11-ol* (**4**). $[\alpha]_D^{20} + 4.9°$ ($c = 1.15\%$, $CHCl_3$). – ^{1}H-NMR.: 0.97 (*d*, $J = 6.5$, 3 H); 1.18 (*s*, 6 H); 1.80 (*s*, 3 H); 2.53 (br., 1 H); 5.40 (1 H), see *Figure*. – MS.: 161 (100), 59 (87), 107 (82), 81 (79), 204 (75, $M^+ - 18$), 189 (69), 93 (64), 105 (63), 162 (52), 95 and 41 (44), M^+ (0).

(±)-(Z)-*Dihydrofarnesal* (*Z*-**11**). A solution of (*Z*)-nerolidol (*Z*-**10**, 10 g) in CH_2Cl_2 (150 ml) and sodium acetate (1.2 g) was treated with pyridine chlorochromate [22] overnight. The mixture was poured onto a solution of excess $NaHSO_3$, and the product extracted into pentane. Washing and concentrating gave 5.1 g of farnesals, b.p. 87–104°/0.01 Torr, contaminated with a little unchanged nerolidol (GC.) [^{1}H-NMR.: 1.62 (*s*, 3 H); 1.70 (*s*, 6 H); 5.13 (br. *t*, 2 H); 5.90 (*d*, $J = 7$, 1 H); 9.95 (*d*, $J = 7$, H–C(1), 2*Z* isomer), and 10.05 (*d*, $J = 7$, 2 *E* isomer)]. Based on the H–C(1) signal, there was *ca.* 40% (2*Z*) and 60% (2*E*) isomer. Small pieces of sodium (1.2 g in all) were dissolved in liquid ammonia (100 ml) and ether (100 ml), at the same time adding (6*Z*)-farnesals (5.0 g) dropwise over 30 min. After a further 15 min, the blue colour was destroyed with alcohol and the ammonia allowed to evaporate, replacing it continuously with ether (*ca.* 100 ml). The thereal solution was washed (NH_4Cl, water), concentrated, and purified (GC.). There were many products present (dihydrofarnesal, dihydrofarnesol, some hydrocarbons). Purification (GC., *Carbowax*) yielded a small amount of material with the properties of (*Z*)-dihydrofarnesal. – ^{1}H-NMR.: 0.93 (*d*, $J = 6$, 3 H); 1.59 (*s*, 3 H); 1.65 (*s*, 6 H); 5.60 (br. *t*, 2 H); 9.73 (*t*, $J = 2.5$, 1 H). – MS.: 69 (100), 41 (52), 109 (29), 81 (17), 67 (16), 55 (15), 123 and 93 (13), 43 (12) ... 222 (1, M^+).

(±)-(E)-*Dihydrofarnesal* (*E*-**11**) was made in the same way from (*E*)-nerolidol (*E*-**10**); it had a longer retention time on GC. (*Carbowax*), and the following spectra. – ^{1}H-NMR.: 0.93 (*d*, $J = 6$, 3 H); 1.55 (*s*, 6 H); 1.65 (*s*, 3 H); otherwise similar signals to the *Z*-isomer. – MS.: 69 (100), 41 (52), 109 (37), 67 and 43 (19), 81 (18), 123 (17), 93 (14), 107 (13) ... 222 (1, M^+).

(±)-(Z)-*Dihydrofarnesol* (**3**). (*Z*)-Dihydrofarnesal (*Z*-**11**) (0.1 g) was reduced in ether (10 ml) with $LiAlH_4$ (0.05 g). The reagent was decomposed with a few drops of water, the mixture was filtered and concentrated, and the product was purified by GC. (*Carbowax*), when it had identical retention times and spectra (^{1}H-NMR., MS.) as the natural (–)-**3**.

The following catalysts were examined for the direct hydrogenation of a farnesol mixture: PtO_2 (*Adams'*), *Raney* Ni, 10% Pd/C and 10% Pt/C. Of these, only the latter gave 2,3-dihydrofarnesols without

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[7]) This signal, measured on a mixture of α- and β-eudesmols which we were unable to separate by GC., is at somewhat higher field than that given by *Pinder* [21].

excessive further reduction. Using this catalyst (0.11 g) in ethanol (110 ml) and a mixture of farnesols (11.1 g), 1.24 l H_2 was absorbed in 4.5 h (theory, 1.12 l). Filtration and concentration yielded a mixture containing *ca.* 80% of dihydrofarnesols, together with unchanged farnesols and a small amount of further reduced material. Preparative GC. *(Carbowax)* yielded pure *Z*- and *E*-isomers of the dihydrofarnesols.

(±)-(E)-*Dihydrofarnesol* was made in the same way (method A) as the *Z*-isomer from (*E*)-dihydrofarnesal. It had a longer retention time (GC., *Carbowax*) and the following spectra: ^{1}H-NMR.: 0.91 (*d*, $J = 6$, 3 H); 1.62 (*s*, 6 H); 1.95–2.1 (br. *s*, *ca.* 6 H). Other signals and the MS. were practically identical with those of the *Z*-isomer.

We thank Mme *Renée Guntz-Dubini* for assistance in the preparation of the dihydrofarnesols, and *Walter Thommen* for assistance in the measurement and interpretation of the ^{13}C-NMR. spectra.

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