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PRENYLATION-CYCLISATION OF GERANYL ACETATE

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Abstract: Conditions have been found for the reaction of α-dimethyl allyl alcohol with geranyl acetate under acid catalysis to give 1,3,3-trimethyl-4-(3 methyl-2-buten-1-yl) 2-acetoxymethyl-1-cyclohexanol. Four isomers have been isolated and their structures determined. Controlled dehydration led to α-cis-, α-trans-, β-, γ-cis- and γ-trans-2-prenyl cyclogeraniol. These were oxidized to the corresponding 2-prenyl cyclocitrals.

The transfer of a prenyl residue from a pyrophosphate to isopentenyl derivatives is an important operation in the biosynthesis of terpenoids. Various techniques have been developed to achieve a laboratory version of this reaction.

Prenyl residues can be transferred to olefins at other stages of terpenoids biosynthesis. A case in point is the formation of the C_{45} and C_{50} carotenoids[1,2]: prenylation of lycopene at the 2 positions (carotenoid numbering) leading to the aliphatic or alicyclic higher carotenoids. In a previous work[3] pseudoionone could be prenylated fairly efficiently; the cyclisation however suffered from low yields owing to the necessary protection-deprotection of the remote double bond. More recently pseudoionone could be directly hydroxyprenylated and cyclised to give α-cis, α-trans and β-hydroxyprenyl ionones[4]. Decaprenoxanthine and C.p. 450 could be synthetized from the α-cis and the β-isomers respectively.

Recent progress in the prenylation of olefins[5] opened the possibility of a more efficient access to the C_{18} synthons 2a-c. In fact pseudoionone gave 35% prenylated products (86% on not recovered pseudoionone) when treated with DMVC and FSO_3H in nitromethane. The distribution of products was 1a: 9 (21)%, 1b: 10 (24)%, 2a 5 (14)%, 2b: 7 (11)% and 2c: 3 (12)%. Nearly half of the prenylated products have been cyclized in the same operation. However the isolation of these compounds proved troublesome.

We next turned to geranyl acetate. Admittedly it has a C_{10} carbon chain instead of a C_{13} one but it is available in a state of high stereochemical purity. When treated under the same reaction conditions, it was prenylated mainly on the distant double bond (conversion 60%). The main compounds formed were the isomeric hydrated prenyl cyclogeranyl acetates 4abcd and some prenyl cyclogeranyl acetates. The open chain diolacetate 5a and trienester 5c resulted from prenylation at the 6 position, whereas the attack of the nearer double bond led to the diolacetates 6ab and the

trienester 6c.

TABLE 1. Prenylation of geranyl and neryl acetate in nitromethane with DMVC (1 eq)

	Conversion %	4abcd %	5a % or 5b*	5c % or 5d*	6ab %	6c %	8** %	Total Prenylation %
Geranyl acetate FSO_3H, 0.08 eq.	60	19 (32)	5 (9)	8 (13)	6 (10)	< 2	11 (19)	51 (86)
Geranyl acetate TFAH, 1.25 eq	54	26 (47)	5 (10)	4 (8)	6 (11)	< 2	8 (14)	51 (94)
Neryl acetate TFAH, 1.25 eq	48	13 (28)	6 (12)*	5 (10)*	5 (10)	< 2	6 (12)	37 (76)

* 5b and 5d are Z isomers obtained from neryl acetate
** acetates of sesquicyclogeraniol 8abcde.

Methanesulfonic (0.3 eq), sulfuric acid (0.2 eq) and tetrafluoroboric acid (ether complex 0.6 eq) gave similar results whereas trifluoroacetic acid yielded a somewhat higher proportion of hydroxylated cyclised products (TABLE 1). Six compounds could be isolated by chromatography, the others were identified by comparison (glc) with authentic samples prepared from known compounds (see experimental part).

The cyclic products 4abcd (in the order of increasing polarity) showed only one double bond in the ^{13}C NMR spectrum and two singlets at about 1 ppm in the ^{1}H NMR spectrum as expected for the gem dimethyl group[6]. The stereochemistry of these compounds is described with respect to the acetoxymethyl group. The first prefix indicates the relationship with the prenyl side chain and the second that with the hydroxyl group. The first relation could be ascertained from the presence in the ^{13}C NMR spectrum of 4a and 4d of a CH_3 singlet under 20 ppm which denotes the cis geometry[7,3], whereas compounds 4b and 4c would have the trans configuration.

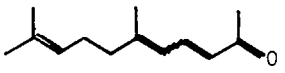
The stereochemistry of the hydroxyl group was deduced by comparison with the related pair 7a 7b[8,9] which shows the same difference: 4a and 4b are higher melting and less polar (in tlc) than 4c and 4d. In the cis-cis isomer, and the cis-trans one, the side chains on C_2 and C_6 could probably be both equatorial, an OH group on C_5 would therefore be axial in the cis-cis and equatorial in the cis-trans one. The IR spectra show in fact a band at 950 for 4a (OH axial) and a 1 055 for 4d[10] (OH equatorial).

In the ^{13}C NMR spectrum of 4a the equatorial methyl on C_5 is found at a lower field than the axial one in 4d where it is shielded by one of the geminal methyl groups. This methyl group appears at 28.2 or 23.7 in 4a and 4d respectively.

The differences in conformational energy between the conformers of 4b and 4c will be smaller. The conformers with the axial OH groups will be expected to be slightly favoured by about 6 Kj/mole[11]. The shielding of the 5a methyl group in the ^{13}C NMR spectrum of 4c is in agreement with this tentative attribution of configuration. The infrared spectra are also in agreement but the situation is not as clear as with 4a and 4d.

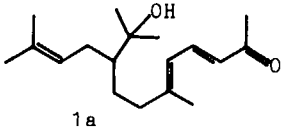
TABLE 2. Composition of the mixtures 4abcd formed in the prenylation of geranyl and neryl acetate

	4a-cis,cis %	4b-trans,cis %	4c-trans,trans %	4d-cis,trans %	selectivity
Geranyl acetate	6.5	4	32.5	57	63,5 cis
Neryl acetate	12.5	79.5	-	8	79,5 trans

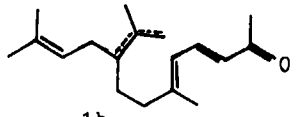


PSEUDOIONONE

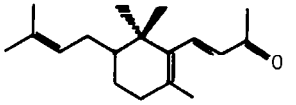
DMVC FSO_3H / CH_3NO_2



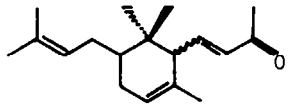
1a



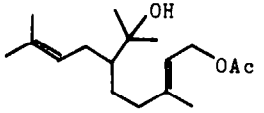
1b



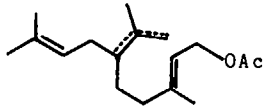
2c



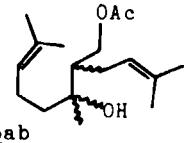
2a : α-cis
2b : α-trans



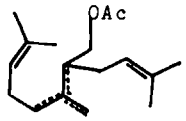
5a:E 5b:Z



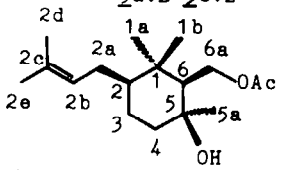
5c:E 5d:Z



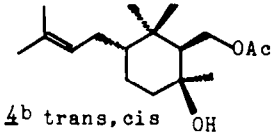
6ab



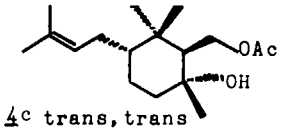
6c



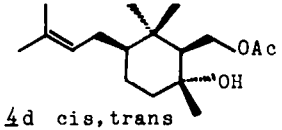
4a cis,cis



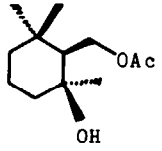
4b trans,cis



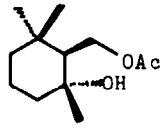
4c trans,trans



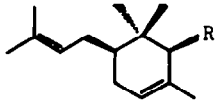
4d cis,trans



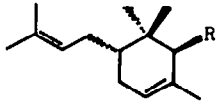
7a



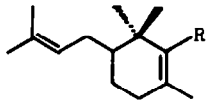
7b



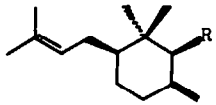
α-cis 8a R=CHOH
9a R=CHO



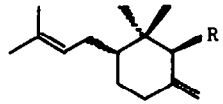
α-trans 8b R=CHOH
9b R=CHO



β 8e R=CHOH
9e R=CHO



γ-cis 8c R=CHOH
9c R=CHO



γ-trans 8d R=CHOH
9d R=CHO

It is to be noted that geranyl and neryl acetates give very different mixtures of isomers 4abcd on prenylation (TABLE 2). The reaction with neryl acetate is much more selective as has been observed already in the acid catalysed cyclisation of the E and Z sulfones related to the irones[12] or in the hydroxyprenylation of E and Z pseudo-ionone[4].

Further, if the configurations of 4abcd are correct, it means that the hydroxyl group entered mainly anti to the attacking carbon electrophile[13]. In the classical view of the polyisoprene cyclisation[14] the prenylation of neryl acetate would involve almost exclusively a chair transition state whereas that of geranyl acetate would show two paths with chair and boat transition states respectively.

The dehydration of hydroxy acetates 4abcd would lead to interesting sesquicyclogeranyl derivatives. The first conditions tried were with phosphorus oxychloride and pyridine[15]. The five isomeric dehydration products have been isolated and characterized (see experimental part). TABLE 3 shows that 4a and 4b were not very reactive and gave almost exclusively the β isomer whereas 4c and 4d were readily dehydrated to mixtures of α and γ derivatives. This agrees with the anti elimination observed previously[16]. The interesting γ-isomer being formed preferentially from precursors having equatorial hydroxyl groups.

TABLE 3. Dehydration of 4abcd

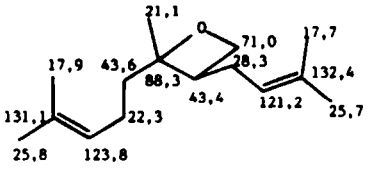
Reagent $POCl_3$ (1.5 eq.), Pyr rt, 36 h	Conversion %	Yield %	α-cis %	α-trans %	β %	γ-cis %	γ-trans %
4a	2	2	20	0	80	0	0
4b	36	35	0	11	84	0	5
4c	98	92	0	43	9	0	48
4d	98	98	28	0	12	60	0
BF_3, AcOH rt, 30 mn*							
4a	32	21	83	0	traces	17	0
4b	92	53	0	81	"	0	19
4c	100	68	0	74	"	0	26
4d	100	72	73	0	"	27	0

*after 3 h the γ-acetates were 87% isomerized into the γ isomers

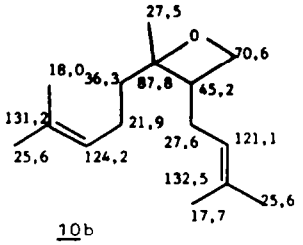
When the dehydration was effected with BF_3, AcOH different results were obtained (TABLE). The β-isomer however is not stable under these reaction conditions, being converted into a C_{15} hydrocarbon. On the other hand it looks as if the configuration at C_6 is retained and the two epimers at C_5 give about the same mixture which would be in agreement with a E_1 mechanism[15]. It will be seen that with proper choice of precursor and experimental conditions any one of the 5 isomers 8a-e can be preferentially formed. Of particular interest is the γ-cis derivative 8c. It will be recalled that the α-cis and β hydroxyprenyl ionones have been secured[4] but an appropriate starting material for the C_{50} carotenoid sarcinaxanthin (with γ-rings) is yet to be prepared. A few other reaction conditions were tried in the hope of increasing the proportion of the valuable γ-cis compound, $POCl_3$-collidine, $SOCl_2$-pyridine, potassium hydrogen sulfate, iodine were tried with no improvement in the results.

The four alcohols 8a-d were oxidized with pyridinium-dichromate[17]. The β isomer 8e was oxidized with manganese dioxide[18].

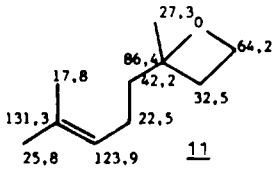
The five isomeric prenyl cyclocitrals have thus been secured. Terminal oxidation with selenium dioxide[19] at some stage in the synthesis should open the way to sarcinaxanthin.



10a



10b



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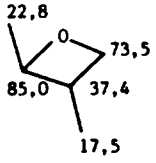

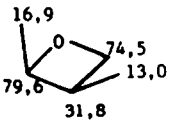

The minor components of the prenylation mixture were also investigated. The diol mono acetate 5a clearly resulted from oxyprenylation of the remote double bond. The isomeric Z compound 5b could be isolated in the prenylation of neryl acetate.

Compound 6ab could be identified from the analytical data as resulting from prenylation at C_2. This is the sort of reaction that leads to the "irregular terpenes" such as presqualene alcohol[20,21]. It has been achieved recently by isomerisation of digeranyl ether with a methyl aluminium aryloxytriflate[22]. Interestingly, compound 6ab contains two isomeric racemates in the proportion 87/13 whereas neryl acetate leads to a mixture of the same compounds in the proportion 12/88. This enabled the isolation of both (racemic) compounds 6a and 6b and showed that the hydroxy prenylation of the 2-3 double bond was almost completely stereospecific. From previous work[23] we surmised that it was anti but more evidence was sought. After saponification with alcoholic sodium hydroxide, the primary hydroxyl groups were tosylated. Treatment with sodium hydride in DMF then gave the corresponding oxetanes 10a and 10b. For comparison purposes 1-acetoxy-3,7-dimethyl-6-octen3-ol[5] was similarly treated to yield 11. The assignment of configuration was based on the signal of the tertiary methyl group which in considerably shifted towards higher field when it is cis to another group on the next carbon atom[24]. Cis and trans-1,2-dimethyl oxetanes are a case in point[25]. The oxetane derived from geranyl acetate was thus given structure 10a (RS/SR) with the new prenyl group cis to the tertiary methyl group. This implies that the oxyprenylation had occurred in the anti fashion. The prenylation of neryl acetate led to the epimeric oxetane 10b (RR/SS); here again the oxyprenylation was anti[26-29].

EXPERIMENTAL PART

For general indications, see preceding paper. Compounds 1a, 1b, 2a, 2b, 2c were described in a previous paper[3]. Authentic samples of 5c, 5d and 6c were prepared by dehydration ($POCl_3$/pyridine) of the corresponding tertiary alcohols 5a, 5b and 6a. Yields in brackets take into account the recovered starting material. For new compounds, the molecular formula means that a correct (± 3%) combustion analysis has been obtained. For some unstable compounds, this could not be done.

Prenylation of pseudoionone. A solution of FSO_3H (65 µl, 1 mmol) in nitromethane (1 ml) was added over 15 mn at 0°C to a solution of pseudoionone (1.92 g, 0.01 mol) and DMVC (0.86 g, 0.01 mol) in nitromethane (25 ml). After stirring for 2 h at 0° the mixture was quenched with aqueous sodium bicarbonate and extracted with ether (3 x 50 ml). After addition of dodecyl acetate (internal standard) the mixture was analysed by gle, the various compounds were identified by comparison with authentic samples[3] and by gle-mass. Several attempts to isolate (MPLC) these compounds in a pure state failed.

Prenylation of geranyl acetate. A solution of TFAH (5 ml, 0.063 mol) in nitromethane (15 ml) was added over 15 mn at 0° to a solution of geranyl acetate (9.8 g, 0.05 ml) and DMVC (4.5 g, 0.05 mol) in nitromethane (125 ml). After stirring for 4 h at 0° the mixture was quenched with saturated aqueous sodium bicarbonate and extracted with ether (3 x 250 ml). After the usual work up the solvent and excess geranyl acetate were distilled off. i.v. (for reuse) and the residue was flash chromatographed on silice 60H (200 g). Elution was performed with gradually enriched mixtures of light petroleum ether/ether (95/5 till 0/100). 100 ml fractions were collected which gave successively compound 5c and 6c the acetates of 8 together with higher prenylation products 1.5 g, about 11 (21)%; a mixture of 4a and 4b, 0.4 g, 3 (5%); compound 6a, 0.8 g, 6 (11)%; 5a, 0.7 g, 5 (10)%; 4c, 1.2 g, 9 (16)%; 4d, 2 g, 14 (26)%.
A second chromatography on a Lobar column with ethyl acetate, petroleum ether (15/85) gave pure compounds.

2-r-Acetoxymethyl-1,3,3-trimethyl-4-c(3-methyl-2-buten-1-yl)-1-c-cyclohexanol 4a

Colorless solid, mp 57°, $C_{17}H_{30}O_3$
IR ($CHCl_3$): 3 670 (f), 3 590 (F), 3 490 (F), 2 970 (F), 2 930 (F), 2 860 (F), 1 730 (F), 1 455 (m), 1 370 (F), 1 240 (F), 1 185 (f), 1 035 (F), 975 (f), 950 (f), 920 (f), 860 (m).
^1H NMR (250 MHz): 5.12 (1H, t); 4.44 and 4.32 (2H, part AB of an ABX system, J_{AX} = 5 Hz, J_{BX} = 2.5 Hz, J_{AB} = 12.5 Hz); 2.23-2.03 (2H, m); 2.06 (3H, s); 1.76-1.19 (7H, m); 1.71 (3H, s); 1.60 (3H, s); 1.21 (3H, s); 1.03 (3H, s); 0.86 (3H, s).
^{13}C NMR: see table
m/e: 264 (M-H_2O, 1%), 204 (M-CH_3CO_2H, 3%), 189 (-CH_3, 8%), 161 (14), 137 (14), 135 (44), 123 (16), 122 (14), 121 (14), 109 (18), 107 (21), 95 (64), 93 (31), 91 (10), 81 (31), 79 (20), 77 (10), 71 (21), 69 (100), 67 (35).

2-r-Acetoxymethyl-1,3,3-trimethyl-4-t(3-methyl-2-buten-1-yl)-1-c-cyclohexanol 4b

Colorless solid, mp 52°, $C_{17}H_{30}O_3$
IR ($CHCl_3$): 3 640 (f), 3 595 (f), 3 460 (f), 2 970 (F), 2 930 (F), 2 880 (m), 1 730 (F), 1 455 (m), 1 370 (m), 1 240 (F), 1 040 (m), 975 (f), 950 (f), 905 (f).
^1H NMR (250 MHz): 5.09 (1H, t); 4.45 and 4.30 (2H, part AB of an ABX system, J_{AX} = 5 Hz, J_{BX} = 3Hz, J_{AB} = 12 Hz); 2.21-1.83 (3H, m); 2.07 (3H, s); 1.67-1.15 (6H, m); 1.71 (3H, s); 1.62 (3H, s); 1.25 (3H, s); 1.12 (3H, s); 0.98 (3H, s).
^{13}C NMR: see table
m/e: 282 (M, 0.5%), 264 (M-H_2O 1%), 204 (M-CH_3CO_2H 3%), 189 (2), 164 (9), 161 (5), 148 (23), 135 (100), 123 (10), 121 (10), 109 (23), 107 (23), 95 (82), 93 (25), 91 (10), 81 (35), 79 (20), 77 (10), 71 (22), 69 (90), 67 (30).

2-r-Acetoxymethyl-1,3,3-trimethyl-4-t-(3-methyl-2-buten-1-yl)-1-t-cyclohexanol 4c

Colorless oil, $C_{17}H_{30}O_3$
IR ($CHCl_3$): 3 590 (f), 3 450 (f), 2 970 (m), 2 940 (m), 2 880 (f), 1 730 (F), 1 460 (m), 1 370 (F), 1 245 (F), 1 050 (f), 1 035 (m), 975 (f).
^1H NMR (250 MHz): 5.07 (1H, t); 4.29 (2H,d,J = 4.5 Hz); 2.21-1.91 (2H, m); 2.07 (3H, s); 1.75-1.47 (7H, m); 1.71 (3H, s); 1.62 (3H, s); 1.25 (3H, s); 1.06 (3H, s); 1.00 (3H, s).
^{13}C NMR: see table.
m/e: 264 (M-H_2O, 2%), 204 (M-CH_3CO_2H, 16%), 189 (-CH_3, 24%), 161 (25), 135 (75), 133 (25), 121 (26), 109 (25), 107 (48), 105 (19), 95 (60), 93 (54), 91 (20), 81 (30), 79 (25), 77 (13), 69 (100), 67 (32).

2-r-Acetoxymethyl-1,3,3-trimethyl-4-c(3-methyl-2-buten-1-yl-t-cyclohexanol 4d

Colorless oil, $C_{17}H_{30}O_3$
IR ($CHCl_3$): 3 660 (f), 3 590 (F), 3 460 (F), 2 970 (F), 2 930 (F), 2 880 (m), 1 730 (F), 1 455 (F), 1 370 (F), 1 245 (F), 1 160 (F), 1 060 (f), 1 035 (m), 975 (m), 920 (m), 845 (m).
^1H NMR (250 MHz): 5.11 (1H, t); 4.41 and 4.34 (2H, part AB of an ABX system, J_{AX} = 5.5 Hz, J_{BX} = 5 Hz, J_{AB} = 12.5 Hz); 2.49 (1H, s); 2.20-2.02 (2H, m); 2.07 (3H, s); 1.83-1.01 (6H, m); 1.71 (3H, s); 1.59 (3H, s); 1.19 (3H, s); 1.05 (3H, s); 0.75 (3H, s).
^{13}C NMR: see table
m/e: 282 (M, 1%); 264 (M-H_2O 1%), 204 (M-CH_3COOH, 7 %); 189 (7), 164 (32), 135 (67), 121 (18), 119 (8), 109 (27), 107 (33), 105 (7), 95 (100), 93 (37), 91 (10), 81 (28), 79 (20), 77 (8), 71 (20), 69 (100), 67 (38).

3,9-Dimethyl-1-acetoxy-6-(1-hydroxy-1-methyl-ethyl)-2E,8-decadiene 5a E

Colorless oil, $C_{17}H_{30}O_3$
IR ($CHCl_3$): 3 600 (F), 3 500 (f), 2 970 (F), 2 930 (F), 2 870 (m), 1 730 (F), 1 450 (m), 1 380 (m), 1 230 (F), 1 030 (m), 960 (m).
^1H NMR (250 MHz): 5.32 (1H, t); 5.18 (1H, t); 4.57 (2H,d,J = 7 Hz); 2.24-1.90 (4H, m); 2.06 (3H, s); 1.67 (6H, s); 1.64 (3H, s); 1.65-1.19 (4H, m); 1.19 (6H, s).
m/e: 264 (M-H_2O) = 0.2%), 204 (3), 189 (6), 161 (12), 137 (18), 135 (10), 124 (23), 123 (23), 121 (13), 109 (27), 107 (15), 105 (5), 96 (25), 95 (35), 93 (30), 81 (75), 79 (23), 69 (60), 68 (30), 67 (33).

5-Acetoxymethyl-2,6,10-trimethyl-2,9-undecadien-6-ol 6a (RS/SR)

Colorless oil, $C_{17}H_{30}O_3$
IR ($CHCl_3$): 3 650 (F), 3 580 (m), 3 500 (m), 3 020 (m), 2 970 (F), 2 920 (F), 2 860 (F), 1 730 (F), 1 450 (m), 1 380 (F), 1 365 (m), 1 240 (F), 1 120 (f), 1 030 (m), 975 (m), 900 (m), 840 (f).
^1H NMR (250 MHz): 5.11 (2H, m); 4.25 and 4.17 (2H, part AB of an ABX system, J_{AX} = 5 Hz,

J_{BX} = 4.5 Hz, J_{AB} = 12 Hz); 2.26-1.98 (4H, m); 2.07 (3H, s); 1.83-1.49 (4H, m); 1.70 (6H, s); 1.63 and 1.61 (6H, s); 1.17 (3H, s).
^{13}C NMR (80 MHz): 170.5 (Ac); 132.6 (>C=); 131.4 (>C=); 124.1 (-C=); 122.4 (-CH=); 74.2 (-C-OH); 64.3 (CH_2O); 46.8 (CH); 40.7 (CH_2); 26.1 (CH_2); 25.9 (CH_3); 25.8 (CH_3); 24.4 (CH_3); 22.2 (CH_2); 21.2 (Ac); 17.8 (2 CH_3).
m/e:264 ($M-H_2O$, 0.5 %), 204 ($M-CH_3COOH$, 4%), 189 (3), 161 (17), 148 (9), 139 (7), 135 (19), 121 (11), 109 (29), 107 (15), 96 (14), 95 (13), 93 (22), 91 (7), 82 (14), 81 (46), 79 (11), 71 (20), 69 (100), 67 (22).

5-Tosyloxymethyl-2,6,10-trimethyl-2,9-undecadien-6-ol (RS/SR)

The acetoxy alcohol 6a (0.68 g, 2.41 mmol) was treated with 1N sodium hydroxide (3 ml) dissolved in ethanol (20 ml). After 4 h at rt the usual work up gave the diol (0.546 g, 94%).
^{1}H NMR (250 MHz): 5.13 (2H, t); 3.72 (2H, m); 2.80 (2H, s); 2.17-1.49 (7H, m); 1.71 (6H, s); 1.65 and 1.61 (6H, 2s); 1.19 (3H, s). The corresponding primary tosylate was obtained by treatment of the preceding diol (0.421 g, 1.75 mmol) with tosyl chloride (0.35 g, 1.8 mmol) in pyridine (5 ml) for 12 h.
Colorless oil, 0.62 g (90%).
^{1}H NMR (250 MHz): 7.75 and 7.31 (4H, 2d, J = 2 Hz); 5.07 and 4.95 (2H, 2t); 4.16 (2H, m); 2.45 (3H, s); 2.14-1.94 (4H, m); 1.76 (1H, s); 1.69, 1.63, 1.61 and 1.56 (12H, 4s); 1.76-1.39 (3H, m); 1.13 (3H, s).

1-Methyl-2-(3-methyl-2-buten-1-yl)-1-(4-methyl-3-penten-1-yl) oxetane 10a (RS/SR)

Sodium hydride (100 mg) was added to the preceding tosylate (0.532 g, 1.41 mmol) in DMF (15 ml). After standing12 h at rt the mixture was hydrolysed and worked up: 0.279 g (93%*).

IR ($CHCl_3$): 2 970 (F), 2 930 (F), 2 870 (F), 1 450 (m), 1 380 (F), 1 240 (F), 1 110 (m), 970 (F), 850 (F).
^{1}H NMR (250 MHz): 5.13 and 4.95 (2H, 2t); 4.51 (1H, dd, J_1 = 6 Hz, J_2 = 8.5 Hz); 4.15 (1H, dd, J_1 = 6 Hz, J_2 = 7 Hz); 2.68 (1H, p); 2.25 (2H, t); 2.00 (2H, dt); 1.75-1.67 (2H, m); 1.75, 1.73 and 1.67 (12 H, 3 s); 1.39 (3H, s).
^{13}C NMR: see above
m/e: 222 (M, 2%), 208 (M-15, 3%), 204 (1), 191 (4), 189 (2), 179 (4), 161 (5), 135 (15), 123 (15), 121 (18), 109 (38), 107 (27), 105 (12), 95 (23), 93 (31), 91 (21), 84 (18), 81 (63), 79 (23), 77 (15), 71 (15), 69 (100), 67 (35).

Prenylation of neryl acetate. The reaction was carried out as with geranyl acetate. Conversion: 48%. The residue (6.9 g) was chromatographed to give successively compounds 5d and 6c, the acetates of 8 together with higher prenylation products 1.6 g, about 12 (25)%; compound 6b, 0.7 g, 5 (10)%; a mixture of 4a and 4b, 1.6 g, 11 (24)%; compound 5b, 0.8 g, 6 (12)%; unidentified compound, 0.4 g, 3 (6)%; compound 4d, 0.3 g, 2 (4)%. Total yield of prenylation products 39 (81)% . 0.75 non identified material was obtained. The various fractions were rechromatographed on a Lobar column to give the individual pure compounds.

1-Acetoxy-6-(1-hydroxy-1-methylethyl)-3,9-dimethyl-2Z, 8-decadiene 5b Z

Colorless oil, $C_{17}H_{30}O_3$
IR ($CHCl_3$): 3 600 (F), 3 500 (f), 2 970 (F), 2 930 (F), 2 870 (m), 1 730 (F), 1 450 (m), 1 380 (m), 1 230 (F), 1 030 (m), 960 (m).
^{1}H NMR (250 MHz): 5.33 (1H, t); 5.20 (1H, t); 4.56 (2H, d, J = 7 Hz); 2.26-1.92 (4H, m); 2.04 (3H, s); 1.76 (3H, s); 1.70 (3H, s); 1.65 (3H, s), 1.66-1.19 (4H, m); 1.19 (6H, s).
^{13}C NMR (80 MHz): 170.3 (Ac); 142.7 (>C=); 131.3 (>C=); 124.0 (-CH=); 118.6 (-CH=); 73.5 (>C-OH); 60.9 (CH_2O); 49.7 (CH); 31.9 (CH_2); 29.3 (CH_2); 29.1 (CH_2); 27.5 (CH_3); 27.2 (CH_3); 25.8 (CH_3); 23.4 (CH_3); 21.0 (Ac); 17.8 (CH_3).
m/e: 264 ($M-H_2O$), 204 (3), 189 (6), 161 (11), 137 (18), 135 (10), 124 (23), 123 (20), 121 (13), 109 (25), 107 (14), 105 (4), 96 (26), 95 (36), 93 (29), 81 (73), 79 (21), 69 (63), 68 (28), 67 (32).

5-Acetoxymethyl-2,6,10-trimethyl-6-hydroxy-2,9-undecadiene 6b (RR/SS)

Colorless oil, $C_{17}H_{30}O_3$
IR ($CHCl_3$): 3 660 (F), 3 590 (m), 3 500 (m), 3 030 (f), 2 970 (F), 2 920 (F), 2 860 (m), 1 730 (F), 1 450 (m), 1 380 (m), 1 365 (m), 1 240 (F), 1 140 (f), 1 030 (m), 975 (m), 910 (f).
^{1}H NMR (250 MHz): 5.09 (2H, m); 4.20 and 4.11 (2H, part AB of an ABX system, J_{AX} = 5 Hz, J_{BX} = 5 Hz, J_{AB} = 12 Hz); 2.33-1.91 (5H, m); 2.05 (3H, s); 1.82-1.47 (3H, m); 1.70 (6H, s); 1.62 (6H, s); 1.19 (3H, s).
^{13}C NMR (80 MHz): 170.4 (Ac); 132.6 (>C=); 131.4 (>C=); 124.0 (-CH=); 122.7 (-CH=); 74.1 (>C-OH); 64.3 (CH_2O); 47.1 (CH); 40.0 (CH_2); 25.9, 25.7, 25.5, 25.0 ($3CH_3$, CH_2); 22.3 (CH_2); 21.1 (Ac); 17.8 ($2CH_3$).
m/e: 264 ($M-H_2O$, 0.2%), 204 ($M-CH_3COOH$, 2%), 189 (3), 161 (10), 148 (6), 139 (4), 135 (14), 121 (8), 109 (22), 107 (12), 96 (12), 95 (13), 93 (19), 91 (5), 82 (40), 81 (5), 79 (11), 71 (18), 69 (100), 67 (19).

5-Tosyloxymethyl-2,6,10-trimethyl-2,9-undecadien-6-ol (RR/SS)

Prepared as for the other isomer (96%)
^{1}H NMR (250 MHz): 5.12 (1H, t); 3.76 (2H, m); 2.78 (2H, s); 2.15-1.89 (4H, m); 1.69 (6H, s); 1.63 and 1.62 (6H, s), 1.65-1.41 (3H, m), 1.29 (3H, s).
The corresponding primary tosylate was prepared as above (88%)
^{1}H NMR (250 MHz): 7.75 and 7.31 (4H, 2d, J = 2 Hz); 5.00 and 4.89 (2H, 2t); 4.05 (2H, d); 2.45

(3H, s); 2.19-1.87 (5H, m); 1.65, 1.59, 1.55 and 1.51 (12H, 4s); 1.65-1.33 (3H, m); 1.13 (3H, s).

1-Methyl-2-(3-methyl-2-buten-1-yl)-1-(4-methyl-3 penten-1-yl)oxetane 10b RR/SS

Colorless oil (88%), $C_{15}H_{26}O$
IR ($CHCl_3$): 2 970 (F), 2 930 (F), 2 870 (m), 1 670 (F), 1 450 (m), 1 375 (F), 1 240 (m), 1 110 (m), 970 (F), 845 (F).
^1H NMR (250 MHz): 5.17 and 4.92 (2H, 2t); 4.52 (1H, dd, J_1 = 6 Hz, J_2 = 8 Hz); 4.10 (1H, dd, J_1 = 6 Hz, J_2 = 7 Hz); 2.64 (1H, p); 2.29 (2H, t); 2.11-1.49 (4H, m); 1.72, 1.67 and 1.65 (12H, 3 s); 1.44 (3H, s).
^{13}C NMR: see above
m/e: 222 (M, 0.5%), 208 (1), 204 (2), 191 (3), 189 (2), 179 (3), 161 (5), 135 (12), 123 (16), 121 (17), 109 (32), 107 (25), 105 (10), 95 (30), 93 (31), 91 (17), 81 (81), 79 (20), 77 (12), 71 (18), 69 (100), 67 (28).

Prenyl cyclogeraniols (sequicyclogeraniols)

Cis-1-Hydroxymethyl-2,2,6-trimethyl-3-(3-methyl-2-buten-1-yl)-5-cyclohexene (α-cis-sesquicyclogeraniol) 8a and cis-1-hydroxymethyl-2,2-dimethyl-6-methylene-3-(3-methyl-2-buten-1-yl) cyclohexane, (γ-cis-sesquicyclogeraniol) 8c.
To a solution of hydroxyacetate 4d (1.55 g) in pyridine (15 ml) phosphorus oxychloride (0.78 ml, 1.5 eq) was slowly added. The reaction mixture was worked up after 12 h to give a mixture of acetates (1.31 g, 28% α-cis, 60% γ-cis, 12% β). This was saponified with 8 ml of 1N sodium hydroxide and 40 ml alcohol for 4 h at rt. The alcohols (1.08 g, 98%) were chromatographed under medium pressure on a Merck Lobar column with iPr_2O/light petroleum/iPrOH (8/91.5/0.5) as eluent.

α-cis-isomer 8a, $C_{15}H_{26}O$.
IR ($CHCl_3$): 3 610 (m), 3 445 (m), 2 970 (F), 2 920 (F), 2 880 (F), 1 670 (f), 1 455 (F), 1 380 (F), 1 370 (F), 1 095 (m), 1 080 (m), 1 010 (m), 990 (m), 950 (m), 850 (m).
^1H NMR (250 MHz): 5.56 (1H, broad s), 5.11 (1H, t), 3.94 and 3.82 (2H, part AB of an ABX system, $J_{AX} = J_{BX}$ = 4 Hz, J_{AB} = 11.5 Hz), 2.26-1.93 (3H, m); 1.87 (1H, s); 1.79 (3H, s); 1.69 (3H, s); 1.59 (3H, s), 1.35-1.21 (3H, m); 1.06 (3H, s); 0.80 (3H, s).
^{13}C NMR: see table
m/e: 222 (M, 4%), 207 (M-CH_3, 6%), 204 (2%), 191 (6), 189 (4), 177 (2), 135 (28), 123 (23), 121 (55), 119 (17), 109 (72), 107 (57), 105 (26), 95 (28), 93 (41), 91 (38), 81 (31), 79 (28), 77 (23), 69 (100), 67 (34).

γ-cis-isomer 8c, $C_{15}H_{26}O$
IR ($CHCl_3$): 3 590 (m), 3 450 (m), 3 080 (F), 2 970 (F), 2 940 (F), 2 860 (F), 1 640 (F), 1 455 (m), 1 390 - 1 370 (m), 1 190 (m), 1 060 (F), 955 (m), 900 (F).
^1H NMR (250 MHz): 5.11 (1H, t); 5.0 and 4.05 (1H, 2s), 3.92 and 3.86 (2H, part AB of an ABX system, J_{AX} = 4 Hz, J_{BX} = 9.5 Hz, J_{AB} = 10 Hz); 2.39-1.75 (5H, m); 1.70 (3H, s); 1.59 (3H, s); 1.65-1.13 (4H, m); 1.09 (3H, s); 4.62 (3H, s).
^{13}C NMR: see table
m/e: 222 (M, 1%), 207 (M-CH_3 2 %), 205 (1), 204 (1), 191 (2), 189 (2), 135 (15), 121 (9), 109 (18), 107 (23), 105 (28), 95 (17), 93 (34), 91 (21), 81 (23), 79 (29), 77 (19), 69 (100), 67 (30).

Trans-1-Hydroxymethyl-2,2,6-trimethyl-3-(3-methyl-2-buten-1-yl)-5-cyclohexene (α-trans sesquicyclogeraniol) 8b and trans-1-hydroxymethyl-2,2-dimethyl-6-methylene-3-(3-methyl-2-buten-1-yl) cyclo hexane, (γ-trans-sesquicyclogeraniol) 8d.
When alcohol acetate 4c was treated as above a mixture of alcohols was obtained (92%), α-trans 43%, γ-trans 48%, β 9%).

α-trans-isomer, 8b $C_{15}H_{26}O$
IR ($CHCl_3$): 3 620 (m), 3 445 (m), 3 000 - 2 845 (F), 1 670 (F), 1 650 (f), 1 450 (F), 1 380 (F), 1 370 (F), 1 185 (f), 1 050 (m), 1 011 (m), 965 (m), 850 (m).
^1H NMR (250 MHz): 5.57 (1H, s); 5.10 (1H, t); 3.75 (2H, d); 2.25-1.44 (6H, m); 1.73 (3H, s); 1.67 (3H; s); 1.58 (3H, s); 1.49 (1H, s); 1.06 (3H, s); 0.81 (3H, s).
^{13}C RMN: see table
m/e: 222 (1), 207 (26), 204 (10), 191 (8), 189 (15), 135 (38), 123 (23), 121 (67), 119 (18), 109 (47), 107 (67), 105 (32), 95 (25), 93 (43), 91 (51), 81 (27), 79 (28), 77 (27), 69 (100), 67 (22).

γ-trans-isomer, 8d $C_{15}H_{26}O$
IR ($CHCl_3$): 3 550 (m), 3 450 (m), 3 070 (f), 2 970 (F), 2 940 (F), 2 880 (F), 1 640 (F), 1 455 (f), 1 390 (m), 1 370 (m), 1 190 (m), 1 170 (m), 1 040 (F), 1 020 (F), 950 (f), 910 (f).
^1H NMR (250 MHz): 5.09 (1H, t); 4.92 and 4.76 (2H, 2s); 3.70 and 3.66 (2H, part AB of an ABX system, J_{AX} = 10.5 Hz; J_{BX} = 5.5 Hz, J_{AB} = 10 Hz); 2.19-1.70 (5H, m); 1.68 (3H, s); 1.57 (3H, s); 1.41 (1H, s); 1.35-1.00 (3H, m); 0.98 (3H, s); 0.84 (3H, s).
^{13}C NMR: see table
m/e: 222 (M, 1%), 207 (M-CH_3 6%), 204 (7), 189 (8), 177 (9), 161 (6), 135 (20), 123 (28), 121 (22), 109 (31), 107 (41), 105 (12), 95 (20), 93 (45), 91 (26), 81 (41), 79 (28), 77 (18), 69 (100), 67 (24).

1-Hydroxymethyl-2,2,6-trimethyl-3-(3-methyl-2-buten-1-yl)-6-cyclohexene (β-sesquicyclogeraniol) 8e

The dehydration of hydroxyacetate 4b gave (93%) a mixture of acetates (15% α-trans and 85% β). After saponification the β isomer was isolated by chromatography on a Lobar column. $C_{15}H_{26}O$.
IR ($CHCl_3$): 3 605 (m), 3 445 (m), 3 000-2 850 (F), 1 650 (f), 1 455 (m), 1 390 (m), 1 380 (m), 1 370 (m), 985 (F),
^1H NMR (250 MHz): 5.10 (1H, t); 4.20 and 4.11 (2H, 2d, J = 12.5 Hz); 2.21-1.89 (4H, m); 1.76 (3H, s); 1.71 (3H, s); 1.60 (3H, s); 1.37-1.15 (3H, m); 1.11 (3H, s); 1.06 (1H, s); 0.89 (3H, s).

^{13}C RMN: see table
m/e: 222 (M, 1%), 207 (M-CH_3, 7,5%), 204 (M-H_2O, 5%), 189 (7), 161 (6), 135 (21), 121 (31), 109 (22), 107 (40), 105 (16), 95 (26), 93 (54), 91 (3), 81 (52), 79 (33), 77 (25), 69 (100), 67 (32).

Sesquicyclocitrals

In a flask were placed successively the cyclic alcohol 8a-d, (330 mg, 1.5 mmol) and pyridinium dichromate (1 070 mg, 3 mmol) in dichloromethane (20 ml). The mixture was stirred at rt for 15 h; after addition of ether (60 ml) it was filtered on celite. After distillation of the ether the residue was taken up in 1,2-dichloroethane and evaporated (yield: 85-90%). Analytical samples were purified by flash chromatography (3 g silice 60 H, light petroleum/ether (95/5)) yield 60-65%.

1-Formyl-2,2,6-trimethyl-3-cis-(3-methyl-2-buten-1-yl)-5-cyclohexene, (α-cis-sesquicyclocitral) 9a

IR ($CHCl_3$): 2 980 (F), 2 930 (F), 2 890 (F), 2 870 (f), 2 740 (m), 1 720 (F), 1 675 (m), 1 450 (m), 1 375 (m), 1 110 (f), 920 (F).
^1H NMR (250 MHz): 9.62 (1H, d, J = 5 Hz); 5.65 (1H, s); 5.07 (1H, t); 2.55 (1H, s); 2.14 (2H, m); 1.86-1.00 (m, 3H); 1.67, 1.62 and 1.59 (9H, 3s); 1.03 and 0.95 (6H, 2s)
^{13}C NMR: see table
m/e: 220 (M, 5%), 205 (M-15, 4%), 191 (2), 187 (3), 177 (4), 162 (4), 149 (4), 135 (10), 133 (7), 123 (24), 121 (62), 109 (31), 107 (42), 105 (19), 95 (22), 93 (20), 91 (38), 81 (38), 70 (25), 77 (24), 71 (12), 69 (100), 67 (31),

1-Formyl-2,2,6-trimethyl-3-trans-(3-methyl-2-buten-1-yl)-5-cyclohexene(α-trans-sesquicyclocitral) 9b

IR ($CHCl_3$): 2 980 (F), 2 930 (F), 2 890 (F), 2 840 (m), 2 740 (m), 1 715 (F), 1 675 (m), 1 450 (m), 915 (F).
^1H NMR (250 MHz): 9.57 (3H, d, J = 5 Hz); 5.74 (1H, s); 5.13 (1H, t); 2.35 (1H, d, J = 5 Hz); 2.24 (2H, m); 1.87-1.54 (3H, m); 1.70, 1.61 and 1.58 (9H, 3s); 1.04 (3H, s); 0.84 (3H, s).
^{13}C NMR: see table
m/e: 220 (M, 20%), 205 (M-15, 9%), 191 (5), 187 (4), 177 (8), 175 (4), 151 (5), 150 (5), 149 (22), 135 (12), 133 (13), 123 (10), 121 (40), 119 (7), 109 (16), 107 (15), 105 (7), 95 (12), 93 (10), 91 (15), 81 (18), 79 (12), 77 (14), 69 (100), 67 (15).

1-Formyl-2,2-dimethyl-3-cis-(3-methyl-2-buten-1-yl)-6-methylene cyclohexane (γ-cis-sesquicyclocitral) 9c

IR ($CHCl_3$): 3 080 (F), 2 970 (F), 2 940 (F), 2 870 (F), 2 740 (m), 1 715 (F), 1 645 (m), 1 470-1 440 (m), 1 390 (m), 1 375 (m), 1 170 (f), 1 100 (f), 900 (F).
^1H NMR (250 MHz): 9.67 (1H, d, J = 5 Hz); 5.10 (1H, t); 4.96 and 4.54 (2H,s); 2.56 (1H, d, J = 5 Hz); 2.39-1.73 (4H, m); 1.73 (3H, s); 1.61 (3H, s); 1.33-1.13 (3H, m); 1.05 (3H, s); 100 (3H, s).
^{13}C NMR: see table
m/e: 220 (M, 12%), 205 (M-CH_3, 23%), 191 (1), 187 (1), 164 (7), 136 (6), 135 (6), 123 (10), 122 (8), 121 (12), 109 (34), 107 (13), 105 (5), 95 (14), 93 (11), 91 (11), 81 (26), 79 (15), 77 (10), 69 (100), 67 (6).

1-Formyl-2,2,dimethyl-3-trans-(3-methyl-2-buten-1-yl)-6-methylene cyclohexane (γ-trans-sesquicyclocitral) 9d

IR ($CHCl_3$): 3 070 (f), 2 970 (F), 2 940 (F), 2 870 (F), 2 745 (m), 1 715 (F), 1 640 (m), 1 450 (m), 1 390 (m), 1 375 (m), 1 370 (m), 900 (F).
^1H NMR (250 MHz): 9.85 (1H, d, J = 3.5 Hz); 5.10 (1H, t); 4.92 and 4.75 (2H, 2s); 2.71 (1H, d, J = 3.5 Hz); 2.38-2.09 (4H, m); 1.89-1.58 (3H, m); 1.70 (3H, s); 1.58 (3H, s); 1.14 (3H, s); 0.84 (3H, s).
^{13}C NMR: see table
m/e: 220 (M, 7%), 205 (M-CH_3, 4%), 191 (3), 177 (4), 151 (9), 150 (4), 149 (4), 137 (4), 135 (6), 133 (6), 123 (18), 121 (22), 109 (46), 107 (30), 105 (13), 95 (23), 93 (20), 91 (25), 81 (48), 79 (30), 77 (23), 69 (100), 67 (38).

1-Formyl-2,2,6-trimethyl-3-(3-methyl-2-buten-1-yl)-6-cyclohexene (β-sesquicyclocitral) 9e

β-Sesquicyclogeraniol (1.11 g, 5 mmol) was stirred with manganese dioxide[18] (10 g) for 4 h in pentane (50 ml). After filtration through celite and evaporation of the solvent the aldehyde was obtained (1.01 g, 91%), pale yellow liquid.
IR ($CHCl_3$): 3 030 (F), 2 980 (F), 2 930 (F), 2 880 (F), 1 670 (F), 1 615 (m), 1 455 (m), 1 420 (m), 1 390 - 1 370 (m), 1 290 (m), 1 240 (m).
^1H NMR (250 MHz): 10.14 (1H, s); 5.13 (1H, t); 2.29-2.00 (4H, m); 2.10 (3H, s); 1.80-1.13 (3H, m); 1.72 (3H, s); 1.61 (3H, s); 1.27 (3H, s); 1.09 (3H, s).
^{13}C NMR: see table
m/e: 220 (M, 60%), 205 (M-CH_3, 17%), 191 (5), 187 (4), 177 (11), 151 (11), 149 (12), 137 (22), 135 (18), 133 (21), 123 (39), 121 (41), 119 (10), 109 (43), 107 (30), 105 (15), 95 (28), 93 (22), 91 (24), 81 (81), 79 (27), 77 (20), 71 (13), 69 (100), 67 (34).

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^{13}C NMR SPECTRA

	1	2	3	4	5	6	1a	1b	2a	2b	2c	2d	2e	5a	6a
4a	37.2	48.9	23.1	41.1	71.8	53.7	17.0	28.2	28.9	124.2	131.6	17.9	25.9	31.0	63.1
4b	36.0	45.9	20.1	35.4	71.5	48.4	25.6	28.7	25.1	124.0	130.8	17.8	25.7	31.1	62.9
4c	36.6	44.9	22.5	36.7	72.7	52.2	26.3	26.9	26.4	123.9	131.3	17.9	25.8	27.8	63.6
4d	37.6	48.7	25.4	42.5	72.4	56.5	16.6	23.7	28.5	123.8	131.8	17.9	25.8	28.7	63.1
8a	35.4	44.8	28.1	123.7	133.1	53.3	16.7	27.2	28.4	123.9	131.4	17.9	25.9	22.3	61.3
8b	35.0	39.1	29.6	124.2	131.1	55.0	22.4	26.1	28.5	123.9	131.7	17.9	25.9	22.9	61.3
8c	38.5	48.5	29.8	36.5	147.7	56.5	16.0	26.6	28.6	124.0	131.5	17.9	25.9	106.4	59.5
8d	36.5	42.4	28.4	30.7	147.0	59.2	22.8	26.7	28.6	123.8	131.7	17.9	25.9	112.4	59.2
8e	37.4	45.6	23.3	32.1	133.0	137.6	22.0	26.4	28.7	124.1	131.4	17.8	25.8	19.7	58.8
9a	35.9	43.7	27.5	124.8	127.8	64.3	17.9	27.6	28.4	123.2	132.1	17.9	25.9	22.2	209.2
9b	34.9	39.8	29.6	125.7	126.8	66.5	22.4	25.9	28.0	123.0	132.0	17.9	25.9	21.8	201.6
9c	38.4	48.1	27.7	36.1	144.9	65.3	16.4	27.3	28.4	123.4	132.0	17.9	25.9	109.2	204.4
9d	37.9	43.6	28.1	32.6	142.7	69.7	21.9	26.7	28.1	123.4	131.9	17.9	25.9	113	201.8
9e	36.4	46.4	22.6	35.1	140.5	155.3	21.1	26.1	27.9	123.7	131.9	17.9	25.9	19.5	192.2

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