Stereospecific Synthesis of Homogeranic and Homoneric Acids

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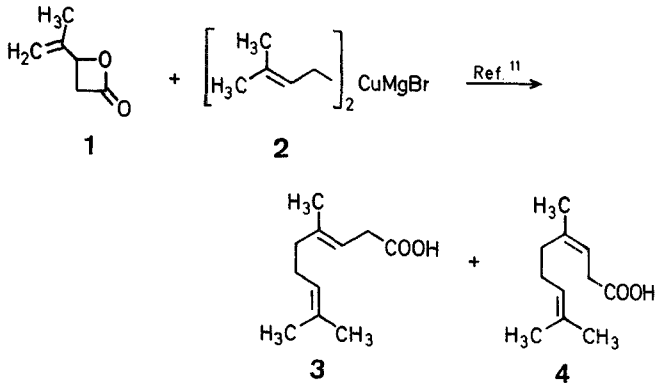
Previously, we studied homogeranic acid **(3)** as a model compound for the electrophilic polyene cyclisation induced by

various reagents[1]. In addition, the acid **3** was used as a precursor in the syntheses of squalene[2], nerolidol[3], di- and tetrahydroactinidiolides[4], ancistrofuran[5], moenocinol[6], dendrolasin[7], and aplysistatin[8].

We have shown[9] that the reported preparation of **3** involving hydroxy/halogen exchange in geraniol and hydrolysis of the intermediale geranyl cyanide[10] in fact affords a 75:25 (*E*)/(*Z*)-mixture of homogeranic (**3**) and homoneric acids (**4**). Similarly, the more recently reported reaction of *β*-isopropenyl-*β*-propiolactone (**1**) with the organocopper reagent **2** yields also a 75:25 mixture of **3** and **4** (Scheme **A**)[11].

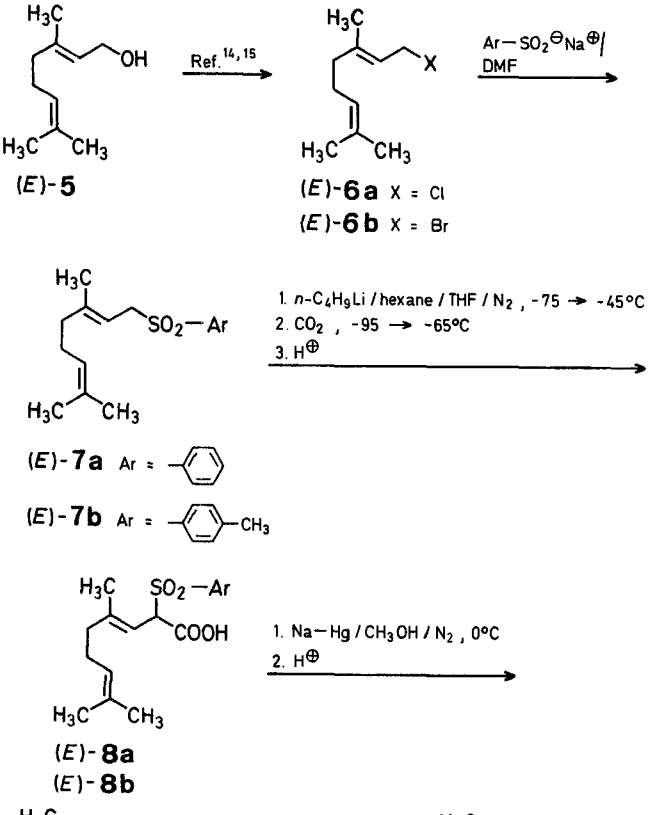


Scheme **A**

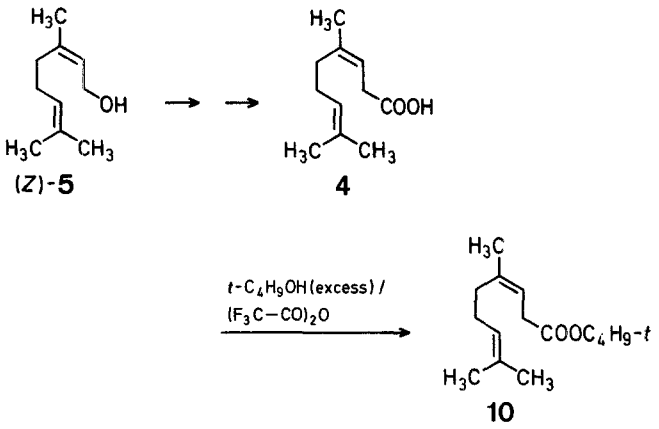
We obtained the pure acid **3** by transformation to the *t*-butyl ester, G.L.C. separation, and subsequent cleavage with trimethylsilyl iodide, or preferably *t*-butyldimethylsilyl trifluoromethanesulfonate[1]. However, this procedure gives only small amounts of **3** and the *t*-butyl ester of the isomeric acid **4** could not be obtained in pure form by G.L.C.

In this communication we describe a stereospecific route for the syntheses of homogeranic acid (**3**) and homoneric acid (**4**). The known sulfone (*E*)-**8a**[12] should give the acid **3** on reductive removal of the arenesulfonyl group, a reaction for which several methods have been developed. Thus, we employed the following sequence starting with geraniol [(*E*)-**5**] to obtain stereochemically pure acid **3** (Scheme **B**).

A similar route starting with the isomeric nerol [(*Z*)-**5**] should afford the (*Z*)-isomeric acid **4** (Scheme **C**).



Scheme **B**



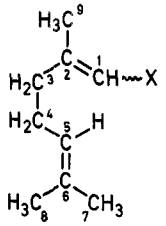
Scheme **C**

The conversion of (*E*)-**5** to the sulfone (*E*)-**7** has already been reported[14,15]. Treatment of (*E*)-**5** with tetrachloromethane/triphenylphosphine gives (*E*)-**6** which is treated with sodium benzenesulfinate in dimethylformamide to give (*E*)-**7a** in 39% yield[14]. Analogously, stepwise reaction of (*E*)-**5** with phosphorus(III) bromide and sodium *p*-toluenesulfinate gives (*E*)-**7b** (yield: 98%, no experimental details given)[15]. Using the latter procedure, we have obtained both (*E*)-**7b** and (*Z*)-**7b** in 91% overall yields starting from geraniol [(*E*)-**5**] and nerol [(*Z*)-**5**], respectively. Under the mild conditions used (ether, 0°C, 15 min), the reactions of **5** with phosphorus(III) bromide are not accompanied by (*E*)/(*Z*)-isomerisations[16]. Furthermore, allylic isomerisations can be excluded by a study of the ^{1}H- and ^{13}C-N.M.R. spectra. In particular, the ^{13}C-N.M.R. spectra show characteristic resonances for the carbon atoms directly bound to the central bond. In the (*E*)-series the methyl group resonates at δ = 16.5 ppm and the methylene group at δ = 40 ppm, whereas in the (*Z*)-series the corresponding resonances are found at 23.5 and 32 ppm, respectively (Table 2)[17].

The poor overall yield reported for (*E*)-**7a**[14] is due to the lower yield in the hydroxy/chlorine exchange (75–81%)[18] and the lower reactivity of (*E*)-**6a** towards sodium benzenesulfinate.

The anions derived from (*E*)- and (*Z*)-**7b** by treatment with *n*-butyllithium[12] are carboxylated to the corresponding (*E*)- and (*Z*)-**8b**. In spite of rigorously anhydrous conditions, complete carboxylation has not been achieved. The disappearance of the deep-red anions is initially rapid but seems to reach a limiting level. Thus the crude products isolated con-

Table 1. ^{1}H-N.M.R. Spectra ($CDCl_3$/TMS)[a], δ [ppm] of Compounds **3**, **4**, (*E*)- and (*Z*)- **6b**, **7b**, **8b**, **9** and **10**



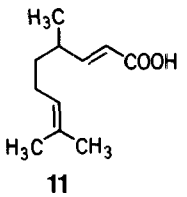
Compound No.	H(1)	H(3)/(4)	H(5)	H(7)	H(8)	H(9)	others (X)
3	5,37 (t, J = 6.8 Hz)	2,06 (br. s)	5,14 (m)	1,68 (s)	1,60 (s)	1,65 (s)	3.09 (d, J = 6.8 Hz, —CH$_2$—COOH); 10.90 (s, COOH)
4	5.42 (t, J = 7.5 Hz)	2.08 (m)	5.19 (m)	1.69 (s)	1.62 (s)	1.77 (s)	3.13 (d, J = 7.5 Hz, —CH$_2$—COOH); 11.88 (s, —COOH)
(*E*)-**6b**	5.63 (t, J = 8.5 Hz)	2.10 (m)	5.16 (m)	1.73 (s)	1.65 (s)	1.76 (s)	4.10 (d, J = 8.5 Hz,—CH—Br)
(*Z*)-**6b**	5.61 (t, J = 8 Hz)	2.15 (m)	5.20 (m)	1.69 (s)	1.65 (s)	1.77 (s)	4.04 (d, J = 8 Hz, —CH$_2$—Br)
(*E*)-**7b**	5.28 (t[b])	2.03 (m)	5.15 (m)	1.70 (s)	1.61 (s)	1.36 (s)	2.46 (s, —CH$_3$); 3.86 (d, J = 8 Hz, —CH$_2$—SO$_2$—Ar); 7.37–8.00 (m, H$_{arom}$)
(*Z*)-**7b**	5.29 (t, J = 8 Hz)	1.83 (br. s)	5.05 (m)	1.66 (s)	1.55 (s)	1.73 (s)	2.44 (s, —CH$_3$); 3.83 (d, J = 8 Hz, —CH$_2$—SO$_2$—Ar); 7.33–7.97 (m, H$_{arom}$)
(*E*)-**8b**	5.35 (d, J = 10.5 Hz)	2.05 (m)	5.13 (m)	1.69 (s)	1.59 (s)	1.51 (s)	2.42 (s, —CH$_3$); 4.91 (d, J = 10.5 Hz, —CH); 7.35–7.95 (m, H$_{arom}$); 10.50 (s, —COOH)
(*Z*)-**8b**	5.35 (d, J = 10.5 Hz)	1.97 (m)	5.08 (m)	1.66 (s)	1.58 (s)	1.80 (s)	2.45 (s, —CH$_3$); 4.90 (d, J = 10.5 Hz, —CH); 7.36–7.96 (m, H$_{arom}$); 11.20 (s, —COOH)
9	5.38 (t, J = 7 Hz)	2.08 (m)	5.16 (m)	1.70 (s)	1.63 (s)	1.63 (s)	1.45 [s, —C(CH$_3$)]; 2.97 (d, J = 7 Hz, —CH$_2$—COO—)
10	5.37 (t, J = 7.5 Hz)	2.03, 2.07 (2 × s)	5.19 (m)	1.68 (s)	1.62 (s)	1.74 (s)	1.43 [s, —C(CH$_3$)$_3$]; 2.97 (d, J = 7.5 Hz, —CH$_2$—COO—)

[a] Measured at 90 MHz on a Varian EM 390 spectrometer.
[b] Partially masked.

tain the desired **8b** together with starting material. The pure acids **8b** are separated by extraction of their sodium salts with 5% aqueous sodium hydroxide followed by acidification. The products (*E*)-**8b** and (*Z*)-**8b** obtained can be recrystallised from pentane and tetrachloromethane, respectively, or used without further purification in the next step.

Reductive cleavage of the sulfone group is readily achieved with 6% sodium amalgam in dry methanol[13]. The generally recommended addition of a phosphate buffer[13], leads to non-reproducible results in this case. To avoid side reactions, the *p*-toluenesulfinic acid formed together with the products **3** and **4**, respectively, should be separated as quickly as possible. This can be achieved by crystallisation from 9/1 cyclohexane/ethyl acetate[19] followed by filtration through a short column of silica gel to remove last traces of the sulfinic acid. In the last step, the products **3** and **4** are obtained in 96% yield.

As previously reported[1], the homogeneity of the acids **3** and **4** can be checked by analytical G.L.C. of the *t*-butyl esters **9** and **10**; the *t*-butyl esters being more suitable for capillary G.L.C. separation (10% Carbowax 20M, Chromosorb WAW80/100, 2 m × 1/8 in 130 °C and SE 30, 25 m) than the corresponding methyl esters. Both acids contain no more than 2% of the other isomer; in marked contrast to the reported synthesis of **3**[10,11]. Additionally, double bond migration to give the conjugated acid **11** is not observed. In the synthesis of **3** via hydrolysis of geranyl cyanide[10], acid **11** is formed as an impurity.



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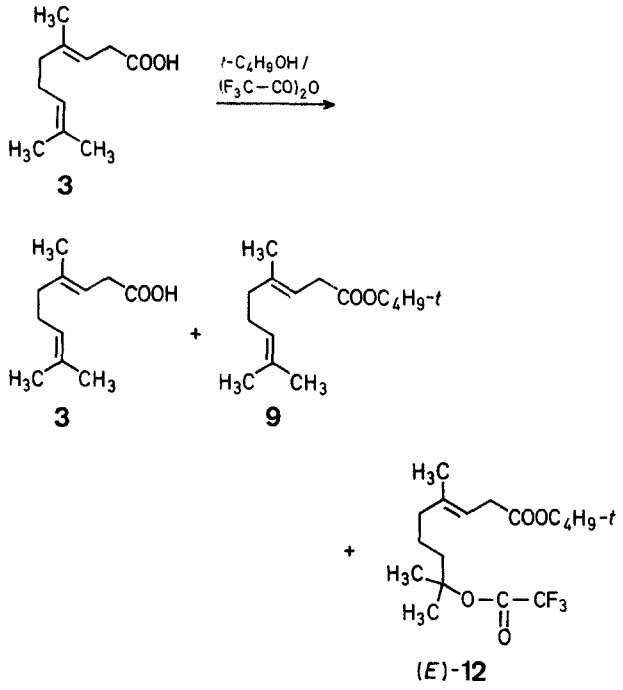
The preparation of the *t*-butyl esters **9** and **10** by the mixed anhydride method[20] proved to be unsatisfactory. Thus, on treatment of a 1:1 mixture of **3** and *t*-butyl alcohol with a five-fold excess of trifluoroacetic anhydride, incomplete reaction is observed and, in addition to **9**, the product of addition of trifluoroacetic acid to the terminal double bond, (*E*)-**12**, is formed in 20% yield (Scheme **D**).

Table 2. ^{13}C-N.M.R. Spectra ($CDCl_3$/TMS)[a], δ [ppm] of Compounds **3**, **4**, (*E*)- and (*Z*)-**8b**, **9** and **10**[b]

Compound No.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	others (X)
3	115.30 (D)	139.69 (S)	39.66 (T)	26.61 (T)	124.09 (D)	131.73 (S)	25.73 (Q)	17.73 (Q)	16.43 (Q)	33.67 (T, $-\underline{C}H_2-$COOH); 178.65 (S, —COOH)
4	116.25 (D)	139.42 (S)	32.27 (T)	26.48 (T)	124.03 (D)	131.87 (S)	25.68 (Q)	17.57 (Q)	23.39 (Q)	33.52 (T, $-\underline{C}H_2-$COOH); 179.17 (S, —COOH)
(*E*)-**8b**	111.92 (D)	134.09 (S)	39.80 (T)	26.16 (T)	123.39 (D)	132.10 (S)	25.65 (Q)	17.63 (Q)	16.85 (Q)	21.64 (Q, $-\underline{C}H_3$); 70.33 (D, —CH); 129.74, 145.39, 147.79 (D, S, S, C_{arom}); 168.83 (S, —COOH)
(*Z*)-**8b**	112.05 (D)	133.97 (S)	32.26 (T)	26.03 (T)	123.00 (D)	132.69 (S)	25.60 (Q)	17.61 (Q)	23.67 (Q)	21.65 (Q, $-\underline{C}H_3$); 70.02 (D, —CH); 129.59, 145.50, 147.91 (D, S, S, C_{arom}); 170.10 (S, —COOH)
9	116.52 (D)	138.44 (S)	39.64 (T)	26.64 (T)	124.19 (D)	131.34 (S)	25.67 (Q)	17.65 (Q)	16.34 (Q)	28.12 (Q, $-C(\underline{C}H_3)_3$); 35.07 (T, $-\underline{C}H_2-$); 80.08 (S, $-\underline{C}(CH_3)_3$); 171.64 (S, —COO—)
10	117.19 (D)	138.52 (S)	32.24 (T)	26.48 (T)	124.09 (D)	131.70 (S)	25.69 (Q)	17.57 (Q)	23.39 (Q)	28.13 (Q, $-C(\underline{C}H_3)_3$); 34.84 (T, $-\underline{C}H_2-$); 80.14 (S, $-\underline{C}(CH_3)_3$); 171.69 (S, —COO—)

[a] Measured at 20 MHz on a Varian FT-80A Spectrometer; abbreviations for CH-Multiplicities S, D, T, Q for singlet, doublet, triplet, quartet due to $^1J_{C,H}$-coupling.

[b] The numbering is the same as for Table 1.



Scheme **D**

In a modifed procedure using a large excess of *t*-butyl alcohol, yields of 88% (for **9**) and 85% (for **10**) are obtained (see experimental section).

In summary, essentially pure stereoisomers **3** and **4** can be prepared on a 10 g scale in 74 and 62% overall yields according to Schemes **B** and **C**.

1-Bromo-3,7-dimethyl-2(*Z*), 6-octadiene [(*Z*)-6b; Neryl Bromide]: A solution of phosphorus(III) bromide (6 ml, 63.8 mmol) in ether (10 ml) is added at 0°C under nitrogen over 5 min to a stirred solution of nerol [(*Z*)-**5**; 21.7 g, 141 mmol] in dry ether (350 ml). After the addition is complete, the solution is stirred for 10 min at 0°C and 10 min after removal of the ice-bath. Saturated brine (350 ml) is added, the organic layer separated, and the aqueous layer extracted with ether (2 × 250 ml). The combined ether extracts are dried with magnesium sulfate. Evaporation of the solvent in vacuo gives (*Z*)-**6b** as a pale yellow liquid which is used without further purification in the next step; yield: 30 g (98%).

By the same procedure, 1-bromo-3,7-dimethyl-2(*E*), 6-octadiene [(*E*)-**6b**; geranyl bromide] is obtained; yield: ~ 100%.

3,7-Dimethyl-1-*p*-tolylsulfonyl-2(*Z*), 6-octadiene (*Z*)-7b: A mixture of neryl bromide [(*Z*)-**6b** 30 g, 138 mmol] and sodium *p*-toluenesulfinate (33.3 g, 155 mmol) in dry dimethylformamide (300 ml) is stirred at room temperature for 24 h. The mixture is then poured on saturated brine (500 ml) and extracted with ether (3 × 300 ml). The ether extracts are combined, washed with saturated brine (3 × 500 ml), dried with anhydrous magnesium sulfate, and concentrated under reduced pressure to yield crude (*Z*)-**7b** which solidifies on standing; yield: 37.5 g (93%); T.L.C.: R_f = 0.58 (cyclohexane/ethyl acetate, 7/3, on silica gel).

As shown by the ^{1}H-N.M.R. spectrum, the product is sufficiently pure to be used in the next step.

Using the same procedure, 3,7-dimethyl-1-p-toluenesulfonyl-2(*E*), 6-octadiene [(*E*)-**7b**] is obtained; yield: 96%; m.p. 42°C (from hexane) (Ref.[17a], m.p. 44°C).

4,8-Dimethyl-2-p-tolylsulfonyl-3(*Z*),7-nonadienoic Acid [(*Z*)-8b]: *n*-Butyllithium (67.2 mmol, 42 ml of 1.6 molar solution in hexane) is added to a stirred solution of the sulfone (*Z*)-**7b** (17.1 g, 58.5 mmol) in tetrahydrofuran (525 ml freshly distilled from benzophenone/sodium ketyl) under nitrogen at −75°C (pentane/liquid nitrogen). The deep-red solution is then stirred for 5 min at this temperature, the cold bath removed for 15 min (temperature rises to −45°C) and the mixture cooled to −95°C (pentane/liquid nitrogen). Carbon dioxide, from a cylinder, is dried by passing first through concentrated sulfuric acid and then through a glass column filled with calcium chloride impregnated with phosphorus pentoxide. It is then introduced to the stirred solution at −95°C over 4 h under a slight posi-

tive pressure of nitrogen. Carbon dioxide introduction is then continued for 1 h while the temperature is allowed to rise slowly to −65 °C. The mixture is then hydrolysed with a saturated ammonium chloride solution (50 ml) and slowly allowed to reach room temperature. The mixture is stirred to facilitate the gentle evaporation of excess carbon dioxide. The aqueous layer is acidified to pH ~ 2 and extracted with ether (3 × 500 ml). The combined ether extracts are washed with saturated brine 1500 ml), dried with anhydrous magnesium sulfate, and the solvent evaporated in vacuo. The crude viscous oil (18.55 g) is shown by ^{1}H-N.M.R. to be a mixture of the acid (*Z*)-**8b** (75%) and starting sulfone (*Z*)-**7b** (25%). It is taken up in ether (500 ml) and extracted with 5% aqueous sodium hydroxide, large quantities of which (2 l) are required to dissolve the resulting sodium salt of (*Z*)-**8b**. The combined basic extracts are acidified with concentrated sulfuric acid, with cooling and stirring, and extracted with ether (3 × 700 ml). The organic layer is dried with anhydrous magnesium sulfate and concentrated in vacuo to give (*Z*)-**8b** as a white powder; yield: 13.95 g (71%). An analytical sample is recrystallised from tetrachloromethane; m.p. 102.5–104 °C.

$C_{18}H_{24}O_4S$	calc.	C 64.25	H 7.20	S 9.53
(336.5)	found	64.01	7.05	9.57

I.R. (Nujol): ν = 1714 cm^{-1}.

Using the same procedure, (*E*)-**7b** is converted to (*E*)-**8b**; yield: 85%; m.p. 103–104 °C (hexane).

4,8-Dimethyl-3(*Z*),7-nonadienoic Acid (4; Homoneric Acid):
Freshly prepared 6% sodium amalgam (33 g; stored under nitrogen in anhydrous cyclohexane) is added in small pieces within 5 min to a vigorously stirred solution of sulfone-acid (*Z*)-**8b** (12.5 g, 37.2 mmol) in anhydrous methanol (400 ml) at 0 °C under nitrogen. After 45 min stirring at 0 °C a second portion of amalgam (41 g, total amount: 74 g, 5.2 equiv) is added. Stirring is continued for 3.5 h at 0 °C and 1 h after removal of the ice-water bath. Mercury and unreacted amalgam are decanted and the solution evaporated to dryness in vacuo. The resulting grey solid is quickly taken up in water (400 ml) and extracted with ether (3 × 200 ml). The basic aqueous phase is acidified (10% sulfuric acid) and extracted with ether (3 × 200 ml). The combined ether extracts are washed with saturated brine (200 ml) and dried with magnesium sulfate. Solvent evaporation in vacuo leaves a crude semi-solid product (11.3 g) which is taken up in cold cyclohexane/ethyl acetate (9/1; 100 ml) and filtered through a Büchner funnel. The white powder is washed with the same mixture and the combined filtrates are concentrated in vacuo to yield 7.7 g of a pale yellow oil which is dissolved in cyclohexane/ethyl acetate (9/1) and filtered through a short column of silica gel (40 g). Solvent removal in vacuo gives **4** as a pale yellow oil; yield: 6.5 g (96%).

I.R. (film): ν = 1711 cm^{-1}.

The white powder was suspected to be *p*-toluenesulfinic acid on the basis of its ^{1}H-N.M.R. spectrum and of that of its ethyl ester recovered after an attempted separation by liquid chromatography using ethyl acetate/hexane as eluent. This spectrum showed a characteristic 16-line multiplet for the methylene group as for the described spectrum of ethyl benzenesulfinate[21]. Recrystallisation from ether affords the *p*-toluenesulfinic acid as long, colourless needles; m.p. 80 °C (Ref.[22], m.p. 86–87 °C).

p-Toluenesulfinic acid; ^{1}H-N.M.R. ($CDCl_3$/TMS) δ = 2.43 (br.s, 3H); 7.32–7.83 (m, 4H$_{arom}$); 10.48 ppm (s, 1H).

Ethyl p-toluenesulfinale; ^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 1.26 (t, 3H, J = 7Hz); 2.41 (s, 3H); 3.95 (ddq, 2H, J = 7Hz, 10Hz); 7.37–7.78 ppm (m, 4H$_{arom}$).

Using the same procedure, (*E*)-**8b** is converted to homogeranic acid **(3)**; yield: 95%; pale yellow liquid.

I.R. (film): ν = 3300–2500, 1700, 1420, 1300, 1215, 940, 825 cm^{-1}.

4,8-Dimethyl-2(E),7-nonadienoic Acid (11):
The acid **11** is obtained by liquid chromatography of the crude reaction mixture from the hydrolysis of geranyl cyanide according to Ref.[10]; yield: 2%.

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 1.06 (d, J = 7Hz, 3H, H_3C—CH); 1.61 (s, 3H); 1.70 (s, 3H); 1.83–2.2 (m, 4H); 2.38 (m, 1H, H_3C—CH); 5.13 [m, 1H, —CH=C(CH$_3$)$_2$]; 5.84 (dd, 1H, M part of AMX, J_{AM} = 16Hz, J_{MX} = 1Hz, =CH—COOH); 7.09 (dd, 1H, A part of AMX, J_{AM} = 16Hz, J_{AX} = 8Hz, —CH=CH—COOH); 11.0 ppm (s, 1H).

I.R. (film): ν = 1708, 1658, 990, 942 cm^{-1}.

***t*-Butyl 4,8-Dimethyl-3(*Z*), 7-nonadienoate (10):**
A solution of homoneric acid (**4**; 2.0 g, 11 mmol) in *t*-butyl alcohol (20 ml) is stirred and cooled in an ice-water bath under nitrogen. Just before crystallisation of the mixture occurs, trifluoroacetic anhydride (7.8 ml, 5 equiv) is added over 10 min via syringe and septum. The mixture is stirred for 5 min and then the cold bath is removed and stirring continued for 45 min. The mixture is poured on 5% aqueous sodium hydrogen carbonate (100 ml) and extracted with ether (2 × 100 ml). The combined ether extracts are dried with anhydrous magnesium sulfate. Evaporation of the solvent in vacuo gives a pale yellow oil (2.6 g), which is purified by liquid chromatography on silica gel with 97/3 cyclohexane/ethyl acetate. The pure ester **10** is obtained as a colourless liquid; yield: 2.21 g (85%).

$C_{15}H_{26}O_2$	calc.	C 75.56	H 11.01
(238.41)	found	75.38	10.92

M.S.: *m/e* (rel. int. %) / 57 (100), 69 (82), 41 (43), 139 (29), 122 (19), 121 (14), 81 (14), 68 (11), 182 (10), 109 (9).

I.R. (film): ν = 1735, 1673, 1369, 1149, 951, 845 cm^{-1}.

By the same procedure, but with a reaction time of only 15 min, homogeranic acid **(3)** is converted in *t*-butyl 4,8-dimethyl-3(*E*),7-nonadienoate **(9)** which is purified by chromatography on silica gel with 97/3 cyclohexane/ethyl acetate.

I.R. (film): ν = 1725, 1145 cm^{-1}.

***t*-Butyl 8-Trifluoroacetoxy-4,8-dimethyl-3(*E/Z*)-nonenoates (*E*)-12 and (*Z*)-12:**
These esters are formed together with **9** and **10**, respectively, when the esterifications are performed according to Ref.[20]. Compound (*E*)-**12** is the only product formed when trifluoroacetic anhydride is added to **3** prior to the addition of *t*-butyl alcohol.

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 1.45 (s, 9H, *t*-C_4H_9); 1.55 [s, 6H, F_3C—CO—O—C(CH$_3$)$_2$—]; 1.63 [br.s, 3H, H_3C—C= in (*E*)-**12**]; 1.74 [br.s, 3H, H_3C—C= in (*Z*)-**12**]; 1.7–2.35 [m, 6H, —CH$_2$)$_3$—]; 2.98 (d, 2H, J = 7Hz, —CH$_2$—COO—); 5.37 ppm (t, J = 7Hz, 1H, =CH—).

I.R. (film): ν = 1780 (CO—CF$_3$), 1735 (CO—OC$_4$H$_9$-*t*); 1220, 1170 cm^{-1}.

G.L.C. Confirmation of the Homogeneity of the Esters 9 and 10:
Purity control by G.L.C. was achieved under the following conditions: (a) capillary column SE 30, 25 m, nitrogen as carrier gas (flow rates; injection: 180 ml/min; detection: 1.5 ml/min), temperature program: 110 to 130 °C (2 °C/min), held for 3 min, 130 to 160 °C (6 °C/min), FID. (b) 10% Carbowax 20M on Chromosorb WAW 80/100, 2 m × 1/8 in, helium as carrier gas (30 ml/min), 130 °C, thermal conductivity detection.

The following retention times were observed: (a) 780 sec for **9**, 730 sec for **10**; (b) 479 sec for **9**, 432 sec for **10**.

By integration (Minigrator, Intersmat Instruments) with both esters the presence of 2% of the other isomer was detected.

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