Acta Chemica Scandinavica B 34 (1980) 391 – 396

Two New Acyclic Diterpenoids from *Nicotiana sylvestris*

INGRID WALLIN, CLAUDINE NARBONNE, INGER WAHLBERG, TOSHIAKI NISHIDA and CURT R. ENZELL

Research Department, Swedish Tobacco Company, P.O. Box 17007, S-104 62 Stockholm, Sweden

Two new acyclic diterpenoids were isolated from *Nicotiana sylvestris* Spegazzini and Comes and shown to be (6*E*,10*E*)-9-hydroxygeneranyllinalool [(6*E*,10*E*)-3,7,11,15-tetramethyl-1,6,10,14-hexadecatetraene-3,9-diol] (*1*) and (3*S*,6*E*,10*E*,14*Z*)-20-hydroxygeneranyllinalool [(2*Z*,6*E*,10*E*,14*S*)-2,6,10,14-tetramethyl-2,6,10,15-hexadecatetraene-1,14-diol] (*2*) by spectral and chemical methods. Solavetivone (*3*) and solanascone (*4*) were also obtained.

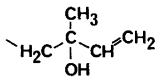
Nicotiana sylvestris Spegazzini and Comes, a plant endemic to northwestern Argentina and considered to be one of the probable progenitors of *N. tabacum* L.,[1] contains fair amounts of the (1*S*,2*E*,4*R*,6*R*,7*E*,11*E*)- and (1*S*,2*E*,4*S*,6*R*,7*E*,11*E*)-2,7,11-cembratriene-4,6-diols (*5*, *6*).[2] During a chromatographic separation of an extract of the leaf wax of this plant with the purpose of isolating these two diols, a few minor constituents were obtained. The present communication describes the isolation and identification of these substances.

RESULTS

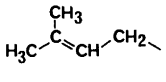
The first isolate (*1*, $C_{20}H_{34}O_2$) was a diol having a tertiary (absorption at 3620 and 3540 cm^{-1} in the IR spectrum of monoacetate *7*) and a secondary hydroxyl group (one proton multiplet at δ 4.46 and at δ 5.62 in the ^1H NMR spectra of *1* and *7* respectively). Since the ^1H and ^{13}C NMR spectra (*cf.* Table 1) demonstrated the presence of four non-conjugated double bonds, of which one was mono- and three trisubstituted, it followed that diol *1* was acyclic.

The monosubstituted double bond, giving rise to a typical ABX system with $J_{AB}=1.5$, $J_{AX}=10.5$ and $J_{BX}=17$ Hz in the ^1H NMR spectrum, was evidently attached to a fully substituted carbon atom, which therefore carried the tertiary hydroxyl group and a methyl group. A comparison of the ^{13}C NMR spectrum of diol *1* with that of linalool (*8*)[3] substantiated and extended this assignment to partial structure A and also inferred the presence in diol *1* of partial structure B.

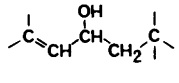
Spin decoupling experiments carried out on acetate *7* after addition of $Eu(dpm)_3$ demonstrated that the secondary hydroxyl group in *1* was present in partial structure C, which was allowed by the ^1H and ^{13}C NMR spectra to be extended to D. Although partial structures A, B and D and the remaining two sp^3 methylene groups can be linked in alternative ways, it seemed most plausible that diol *1* was



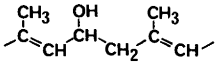
A



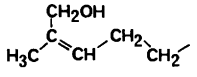
B



C

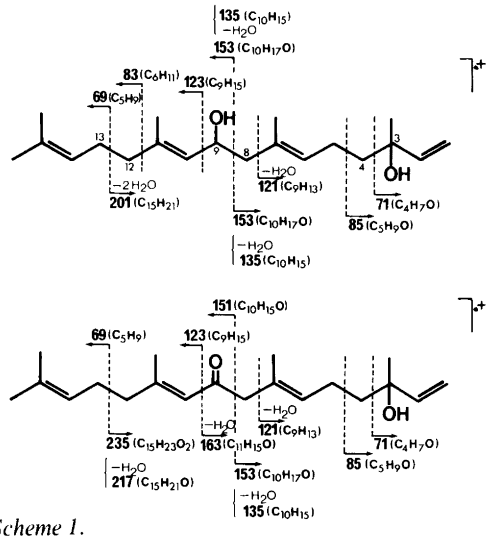


D



E

0302-4369/80/060391-06$02.50

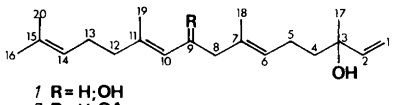


Scheme 1.

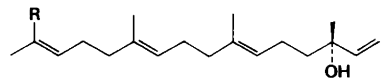
a diterpenoid and had a 9-hydroxygeranyllinalool structure.

The mass spectra of diol *1* and its oxidation product *9*, was in harmony with this assignment. Thus, as illustrated in Scheme 1, the peak at *m/z* 69, which is the base peak in the spectra of both compounds, is associated with breakage of the allylic 12,13 bond and charge retention on the smaller fragment, whereas charge retention on the complementary fragment and dehydration account for the occurrence of the *m/z* 201 and *m/z* 217 peaks in the spectra of *1* and *9* respectively. Fission of the allylic 8,9 bond, a process whose importance is enhanced by the presence of the oxygenated substituent at C-9, explains the generation of the *m/z* 153 and 151 ions from *1* and *9*, respectively, while the *m/z* 71 species, which is produced from both *1* and *9*, arises from an α-cleavage reaction comprising the 3,4 bond.

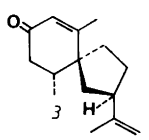
Evidence was also provided by a comparison of the ^{13}C NMR spectra of *1*, *7* and *9* with that of (3*R*,6*E*,10*E*)-geranyllinalool (*10*). Thus, thirteen signals in the spectra of diol *1* and the corresponding monoacetate *7* were of appropriate multiplicities and had chemical shift values virtually identical to those assigned to C-1 to C-5, C-12 to C-18 and C-20 for (6*E*,10*E*)-geranyllinalool (*10*), whereas the spectral congruity between *10* and ketol *9* comprised the C-1 to C-5, C-13 to C-18 and C-20 signals. The shieldings observed for the remaining carbon atoms were readily accounted for by the introduction of a hydroxyl (*1*), and acetoxyl (*7*) and/or oxo (*9*) substituent at C-9 in (6*E*,10*E*)-geranyllinolool (*10*).[4] Moreover, since the chemical shift values of the signals due to C-18, C-19 and C-12 in diol *1*, δ 16.3, 16.6 and 39.6, are diagnostic of the configurations of the 6,7 and 10,11 double bonds,[5] the new constituent of *N. sylvestris* can be formulated as (6*E*,10*E*)-9-hydroxygeranyllinalool [(6*E*,10*E*)-3,7,11,15-tetramethyl-1,6,10,14-hexadecatetraene-3,9-diol] (*1*), the



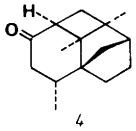
1 R = H;OH
7 R = H;OAc
9 R = O
10 R = H_2



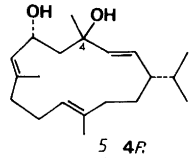
2 R = CH_2OH
11 R = CHO



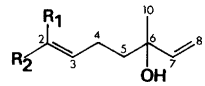
3



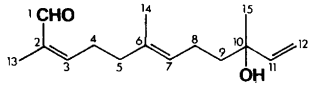
4



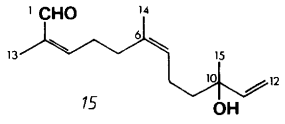
5 4*R*
6 4*S*



8 $R_1 = R_2 = CH_3$
12 $R_1 = CH_2OH$; $R_2 = CH_3$
13 $R_1 = CH_3$; $R_2 = CH_2OH$



14



15

Table 1. Carbon-13 chemical shifts and assignments for compounds *1*, *2* and *7* – *15*.[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19	C-20
1	111.7	145.0	73.3	41.8	23.1	128.5	131.4	48.1	66.2	127.8	137.4	39.6	26.5	124.1	131.3	25.7	28.1	16.3	16.6	17.7
7[c]	111.6	145.1	73.1	42.0	22.8	128.0	131.5	45.4	69.8	123.6	140.1	39.5	26.4	123.9	130.9	25.7	27.8	16.3	16.8	17.7
9	111.7	145.0	73.2	41.8	23.1	122.4	129.8	55.3	199.4	129.4	158.9	41.3	26.2	123.1	132.4	25.7	28.0	16.5	19.4	17.7
10	111.7	145.1	73.5	42.1	22.7	124.2[b]	135.0	39.7	26.6	124.3[b]	135.5	39.7	26.8	124.4	131.2	25.7	27.9	16.0	16.0	17.7
2	111.7	145.0	73.5	42.2	22.8	124.4[b]	135.3	39.6	26.4	124.6[b]	134.4	39.8	26.3	128.1	134.6	21.3	27.7	16.0[b]	16.1[b]	61.3
11	111.7	145.1	73.4	42.1	22.7	124.5	135.2	39.5	26.5	125.5	133.4	38.0	27.4	154.5	139.3	9.2	27.9	16.0	16.0	195.3
8	25.3	130.3	124.6	22.6	41.2	72.7	145.0	111.3	17.5	27.2										
12[6]	61.9	135.3	129.1	22.5	42.3	75.7	145.8	112.3	21.3	28.1										
13[7]	68.3	134.9	125.7	22.4	41.8	73.3	144.9	111.8	13.7	27.6										
14	195.4	139.3	154.6	27.4	37.9	133.6	125.7	22.7	42.0	73.3	145.0	111.7	9.2	15.9	27.7					
15	195.4	139.4	154.4	27.4	30.2	133.4	126.6	22.6	42.3	73.0	145.0	111.7	9.1	23.1	27.7					

[a] δ-Values in $CDCl_3$ relative to TMS. [b] Assignment may be reversed. [c] $OCOCH_3$: 170.2; $OCOCH_3$: 21.2.

chiralities of C-3 and C-9 being unsettled *(vide infra)*.

The second isolate (*2*, $C_{20}H_{34}O_2$) was a diol having a primary (one two-proton singlet at δ 4.12 and one one-proton singlet at δ 9.13 in the ^1H NMR spectra of diol *2* and its oxidation product (*11*), respectively) and a tertiary hydroxyl group (absorption at 3600 and 3500 cm^{-1} in the IR spectrum of *11*). While the NMR and mass spectra were consistent with the allocation of the tertiary hydroxyl group to partial structure A, spin decoupling experiments carried out on aldehyde *11* demonstrated that the primary hydroxyl group in diol *2* formed part of end group E. Since the remaining carbon atoms were present as two trisubstituted double bonds, two methyl groups attached to double bonds and three sp^3 methylene groups, and since a comparison showed that sixteen signals in the ^{13}C NMR spectrum of diol *2* were virtually superimposable on those assigned to C-1 to C-13 and C-17 to C-19 for (6*E*,10*E*)-geranyllinalool (*10*), these results inferred that diol *2* was a 16- or 20-hydroxygeranyllinalool.

Evidence in favour of the latter alternative was provided by the observation that the remaining signals in the ^{13}C NMR spectrum of diol *2* were of appropriate multiplicities and had chemical shift values close to those found for the C-1 to C-3 and C-9 signals for (2*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol (*12*) but characteristically different from those reported for the corresponding signals for the 2*E*-isomer *13*.[6,7]

Supporting evidence was also provided by the striking congruity of the shieldings of the carbon atoms of the comparable end groups in aldehyde *11* and (2*Z*,6*E*)-10-hydroxy-2,6,10-trimethyl-2,6,11-dodecatrienal (*14*)[8] (*cf.* Table 1). Furthermore, the ^{13}C NMR spectra, as illustrated in Table 1 by a comparison of those of *11*, *14* and (2*Z*,6*Z*)-10-hydroxy-2,6,10-trimethyl-2,6,11-dodecatrienal (*15*),[8] are only compatible with a 6*E*,10*E*,14*Z*-configuration in diol *2*.

Moreover, since the measurements of the optical rotations of diol *2*, (*R*)-linalool (*8*) and (3*R*,6*E*,10*E*)-geranyllinalool (*10*) in $CHCl_3$ and methanol, which are detailed in Table 2, are consistent with an *S*-configuration, the second new diol can be identified as (3*S*,6*E*,10*E*,14*Z*)-20-hydroxygeranyllinalool [(2*Z*,6*E*,10*E*,14*S*)-2,6,10,14-tetramethyl-2,6,10,15-hexadecatetraene-1,4-diol] (*2*). Hence, it appears plausible that the configuration at C-3 in diol *1*, (6*E*,10*E*)-9-hydroxygeranyllinalool, is *S* as well.

Table 2. Molecular rotations (Φ) of compounds *2*, *8* and *10* at various wavelengths.

Compound	589 nm $CHCl_2$	MeOH	578 nm $CHCl_3$	MeOH	546 nm $CHCl_3$	MeOH	436 nm $CHCl_3$	MeOH
2	27.5	35.2	30.6	36.7	38.2	42.2	67.9	77.7
10[a]	−29	−31	−33	−39	−41	−41	−48	−58
8	−33.9	−35.0	−35.7	−37.1	−40.6	−42.7	−71.4	−77.0

[a] Due to the low concentration (*c* 0.1) the values measured for (−)-(3*R*,6*E*,10*E*)-geranyllinalool (*10*) are less accurate than those obtained for *2* and *8* (*c* 1.0).

While there are reports of a few naturally occurring oxygenated geranylgeraniols,[9-11] the two new diols of *N. sylvestris* (*1*, *2*) are, to our knowledge, the only hydroxylated geranyllinalools encountered in nature so far.

Solavetivone (*3*), a sesquiterpenoid previously isolated as a stress metabolite of infected potato tubers[12] and as a component of *Nicotiana tabacum*,[13] and solanascone (*4*), a biogenetically related compound found in tobacco,[14] were obtained in low yields from *Nicotiana sylvestris*.

EXPERIMENTAL

With the exception of accurate mass measurements, which were carried out on a Kratos' MS5O-Stereo DS5OSM/DS5OS mass spectrometer-computer system, the instruments specified in Ref. 15 were used.

Isolation. (6*E*,10*E*)-9-hydroxygeranyllinalool (*1*, 300 mg), (3*S*,6*E*,10*E*,14*Z*)-20-hydroxygeranyllinalool (*2*, 80 mg), (−)-solavetivone (*3*, 8 mg) and solanascone (*4*, 2 mg) were isolated from an extract (33 g), obtained by immersing green leaves of *Nicotiana sylvestris* in chloroform, by chromatography over silica gel followed by HPLC using a column packed with μ-Bondapak/CN.

(6*E*,10*E*)-9-Hydroxygeranyllinalool [(6*E*,10*E*)-3,7,11,15-tetramethyl-1,6,10,14-hexadecatetraene-3,9-diol] (*1*) was an oil, $[\alpha]_D$ −6.7° (*c* 0.8 $CHCl_3$); (Found: $(M-18)^{\cdot+}$ 288.2464. Calc. for $C_{20}H_{32}O$: 288.2453); IR (CCl_4) bands at 3620, 3420, 1670, 1645, 1000 and 930 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.29 (3 H, s), 1.61 (3 H, broad s), 1.70 (9 H, m), 4.46 (1 H, dt, *J* = 9 and 7 Hz), 5.10 (1 H, dd, *J* = 1.5 and 10.5 Hz), 5.24 (1 H, dd, *J* = 1.5 and 17 Hz), 5.0−5.4 (3 H, overlapping signals) and 5.94 (1 H, dd, *J* = 10.5 and 17 Hz); MS [*m/z* (%)]: 288 (M−18, 2), 270 (8), 245 (2), 227 (10), 201 (12), 187 (6), 159 (22), 153 (14), 145 (18), 135 (30), 133 (35), 121 (22), 119 (21), 107 (32), 93 (58), 81 (44), 71 (21), 69 (100), 55 (35) and 41 (61).

(3*S*,6*E*,10*E*,14*Z*)-20-Hydroxygeranyllinalool [(2*Z*,6*E*,10*E*,14*S*)-2,6,10,14-tetramethyl-2,6,10,15-hexadecatetraene-1,14-diol] (*2*), was an oil, $[\alpha]_D$ +9.0° (*c* 1.0 $CHCl_3$); (Found: $(M-18)^{\cdot+}$ 288.2450. Calc. for $C_{20}H_{32}O$: 288.2453); IR (CCl_4) bands at 3620, 3350, 3090, 1670, 1645, 1005 and 930 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.29 (3 H, s), 1.61 (6 H, broad s), 1.80 (3 H, d, *J* = 1 Hz), 4.12 (2 H, s), 5.08 (1 H, dd, *J* = 1.5 and 10.5 Hz), 5.23 (1 H, dd, *J* = 1.5 and 17.5 Hz), 5.0−5.4 (3 H, overlapping signals) and 5.94 (1 H, dd, *J* = 10.5 and 17.5 Hz); MS [*m/z* (%, composition)]: 288 (M−18, 2), 270 (2, $C_{20}H_{30}$), 255 (1, $C_{19}H_{27}$), 241 (1, $C_{18}H_{25}$), 203 (5, $C_{15}H_{23}$), 189 (6, $C_{14}H_{21}$), 175 (5, $C_{13}H_{19}$), 161 (12, $C_{12}H_{17}$), 147 (11), 135 (43, $C_{10}H_{15}$), 119 (29, C_9H_{11}), 107 (55, C_8H_{11}), 93 (100, C_7H_9), 81 (50, C_6H_9), 71 (23, C_4H_7O), 69 (33, C_5H_9 and C_4H_5O), 55 (51) and 43 (85).

(−)-Solavetivone (*3*) and solanascone (*4*) were identified by comparison of their IR, NMR and mass spectra with corresponding published data.[12-14]

(−)(3*R*,6*E*,10*E*)-Geranyllinalool (*10*) was isolated from the neutral portion of an ether extract of resin of *Picea abies* by chromatography over silica gel followed by HPLC using columns packed with μ-Bondapak/CN and μ-Porasil. It was identified by comparison of the IR and ^1H NMR spectra with corresponding published data;[16,17] MS [*m/z* (%)]: 290 (M, 2), 272 (6), 257 (2), 245 (1), 229 (3), 221 (3), 203 (12), 189 (6), 175 (2), 161 (13), 147 (10), 137 (12), 135 (25), 123 (10), 107 (25), 93 (48), 81 (49), 71 (15), 69 (100), 55 (13) and 41 (22).

Preparation of (6E,10E)-9-acetoxygeranyllinalool (7). Acetylation using standard conditions converted *1* into (6*E*,10*E*)-9-acetoxygeranyllinalool (*7*), which was an oil and had $[\alpha]_D$ +3° (*c* 0.4 $CHCl_3$) (Found: $(M-60)^{\cdot+}$ 288.2426. Calc. for $C_{20}H_{32}O$: 288.2453); IR (CCl_4) bands at 3620, 3540, 1735, 1670 and 1245 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.28 (3 H, s), 1.61 (3 H, m), 1.63 (3 H, m), 1.71 (3 H, d, *J* = 1 Hz), 2.01 (3 H, s), 2.10 (1 H, dd, *J* = 6.5 and −13 Hz), 2.33 (1 H, dd, *J* = 7 and −13 Hz), 5.07 (1 H, dd, *J* = 1.5 and 11 Hz), 5.21 (1 H, dd, *J* = 1.5 and 17 Hz), 5.0−5.3 (3 H, overlapping signals), 5.62 (1 H, ddd, *J* = 6.5, 7 and 9 Hz) and 5.92 (1 H, dd, *J* = 11 and 17 Hz). After addition of $Eu(dpm)_3$ the following spin

decoupling experiments were carried out: irradiation at the frequency of the signal at δ 5.62 converted the two doublets of doublets at δ 2.10 and 2.33 into an AB quartet ($J = -13$ Hz), while conversely the signal at δ 5.62 collapsed to a doublet ($J = 9$ Hz) when the center of the two doublets of doublets, δ 2.2, was irradiated; irradiation at the frequency of each of the vinylic methyl signals, δ 1.61, 1.63 and 1.71, affected the obscured signals at δ 5.0–5.3, while irradiation of the latter region sharpened the three methyl signals. MS [*m/z* (%, composition)]: 288 (M−HOAc, 5, $C_{20}H_{32}O$), 270 (9, $C_{20}H_{30}$), 255 (4, $C_{19}H_{27}$), 245 (4, $C_{17}H_{25}O$), 227 (12, $C_{17}H_{23}$), 201 (18, $C_{15}H_{21}$), 187 (11, $C_{14}H_{19}$), 175 (9, $C_{13}H_{19}$), 159 (32, $C_{12}H_{15}$), 145 (32, $C_{11}H_{13}$), 135 (63, $C_{10}H_{15}$), 119 (40, C_9H_{11}), 107 (53, C_8H_{11}), 93 (91, C_7H_9), 81 (61, C_6H_9), 71 (30, C_4H_7O), 69 (100, C_5H_9), 55 (42, C_4H_7 and C_3H_3O) and 41 (91).

Preparation of (6E,10E)-9-oxogeranyllinalool (9). To a solution of 25 mg (0.082 mmol) of *1* in dry dioxane was added 28 mg (0.12 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). The reaction mixture was stirred at room temperature for 2 h, evaporated and chromatographed over silica gel to give 15 mg of (6*E*,10*E*)-9-oxogeranyllinalool (*9*), which was an oil (Found: M^{+} 304.2380. Calc. for $C_{20}H_{32}O_2$: 304.2402); λ_{max} 244 nm (ε 12 600, EtOH); IR ($CHCl_3$) bands at 3610, 3500, 1685 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.30 (3 H, s), 1.63 (6 H, m), 1.70 (3 H, m), 2.15 (3 H, d, $J = 1$ Hz), 3.06 (2 H, broad s), 5.08 (1 H, dd, $J = 1.5$ and 10.5 Hz), 5.25 (1 H, dd, $J = 1.5$ and 16 Hz), 5.0–5.4 (2 H, overlapping signals), 5.94 (1 H, dd, $J = 10.5$ and 16 Hz) and 6.09 (1 H, broad s); MS [*m/z* (%)]: 304 (M, 0.2), 286 (2), 271 (1), 261 (1), 243 (1), 233 (1), 217 (5), 203 (1), 181 (2), 163 (6), 151 (53), 135 (8), 123 (27), 109 (14), 95 (15), 81 (21), 71 (8), 69 (100), 55 (23) and 41 (48).

Preparation of (3S,6E,10E,14Z)-20-oxogeranyllinalool (11). To a solution of 10.2 mg (0.033 mmol) of *2* in acetone was added 20 mg (0.23 mmol) of active MnO_2. The reaction mixture was stirred for 5 h, evaporated and chromatographed over silica gel to give 4.2 mg of (3*S*,6*E*,10*E*,14*Z*)-20-oxogeranyllinalool (*11*), which was an oil and had $[\alpha]_D$ +13° (*c* 0.1 $CHCl_3$); (Found: $(M-18)^{+}$ 286.2305. Calc. for $C_{20}H_{30}O$: 286.2297); λ_{max} 227 nm (ε 10 800, EtOH); IR (CCl_4) bands at 3600, 3500, 1685 and 1645 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.29 (3 H, s), 1.61 (6 H, broad s), 1.77 (3 H, four lines, splitting 1.5 Hz), 2.67 (2 H, dt, $J = 7$ and 8 Hz), 5.07 (1 H, dd, $J = 1.5$ and 10.5 Hz), 5.14 (2 H, broad t, $J = 8$ Hz), 5.21 (1 H, dd, $J = 1.5$ and 17 Hz), 5.94 (1 H, dd, $J = 10.5$ and 17 Hz), 6.49 (1 H, tq, $J = 1$ and 8 Hz) and 9.13 (1 H, s); Irradiation at the frequency of the triplet of quartets at δ 6.49 converted the two-proton doublets of triplets at δ 2.67 to a triplet ($J = 7$ Hz) and the four-line system at δ 1.77 to a triplet ($J = 1$ Hz), while conversely the signal at δ 6.49 was converted to a triplet ($J = 8$ Hz) and a quartet ($J = 1$ Hz) when the signals at δ 1.77 and δ 2.67, respectively, were irradiated; irradiation at the frequency of the signal at δ 2.67 also converted the methyl signal at δ 1.77 to a doublet ($J = 0.5$ Hz) and sharpened the signal at δ 9.13, whereas irradiation of the methyl signal at δ 1.77 sharpened the signal at δ 2.67; MS [*m/z* (%)]: 286 (M−18, 4), 271 (1), 258 (1), 203 (4), 175 (2), 161 (9), 147 (9), 135 (62), 119 (19), 107 (43), 93 (100), 81 (53), 71 (35), 69 (33), 55 (78) and 43 (62).

Acknowledgements. We are grateful to Dr. David Jones and Mr. Leif Abrahamsson, who recorded the mass spectra, to Dr. W. W. Reid, Queen Elisabeth College, University of London, who kindly supplied the extracts of *N. sylvestris*, and to Dr. E. Demole, Firmenich SA, Geneva, who provided the samples of the (2*Z*,6*E*)- and (2*Z*,6*Z*)-10-hydroxy-2,6,10-trimethyl-2,6,11-dodecatrienals.

REFERENCES

1. Gray, J. C., Kung, S. P., Wildman, S. G. and Sheen, S. J. *Nature 252* (1974) 226.
2. Reid, W. W. *Ann. Tabac S.E.I.T.A. 2* (1974) 145.
3. Bohlmann, F., Zeisberg, R. and Klein, E. *Org. Magn. Reson. 7* (1975) 426.
4. Wehrli, F. W. and Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*, London 1976.
5. Crombie, L., King, R. W. and Whiting, D. A. *J. Chem. Soc. Perkin Trans. 1* (1975) 913.
6. Tschesche, R., Ciper, F. and Breitmaier, E. *Chem. Ber. 110* (1977) 3111.
7. Behr, D., Wahlberg, I., Nishida, T. and Enzell, C. R. *Acta Chem. Scand. B 32* (1978) 228.
8. Demole, E. and Enggist, P. *Helv. Chim. Acta 56* (1973) 2053.
9. Fattorusso, E., Magno, S., Mayol, L., Santacroce, C., Sica, D., Amico, V., Oriente, G., Piatelli, M. and Tringali, C. *Tetrahedron Lett.* (1976) 937.
10. Ogiso, A., Kitazawa, E., Kurabayashi, M., Sato, A., Takahashi, S., Noguchi, H., Kuwano, H., Kobayashi, S. and Mishima, H. *Chem. Pharm. Bull. 26* (1978) 3117.
11. Francisco, C., Combaut, G., Teste, J. and Prost, M. *Phytochemistry 17* (1978) 1003.
12. Coxon, D. T., Price, K. R., Howard, B., Osman, S. F., Kalan, E. B. and Zacharius, R. M. *Tetrahedron Lett.* (1974) 2921.
13. Fujimori, T., Kasuga, R., Kaneko, H. and Noguchi, M. *Phytochemistry 16* (1977) 392.
14. Fujimori, T., Kasuga, R., Kaneko, H., Sakamura, S. and Noguchi, M. *J. Chem. Soc. Chem. Commun.* (1978) 563.

15. Behr, D., Wahlberg, I., Nishida, T. and Enzell, C. R. *Acta Chem. Scand. B 31* (1977) 573.
16. Demole, E. and Lederer, E. *Bull. Soc. Chim. Fr.* (1958) 1128.
17. Kimland, B. and Norin, T. *Acta Chem. Scand. 21* (1967) 825.

Received January 16, 1980.