30. Biosynthesis of Homoterpenes in Higher Plants

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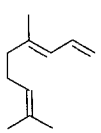
(26.X.88)

In higher plants, the two homoterpenes 4,8-dimethylnona-1,3,7-triene (**1**) and 4,8,12-trimethyltrideca-1,3,7,11-tetraene (**2**) are synthesized from the regular terpene alcohols nerolidol and geranyllinalool by fragmentation into the homoterpene and butenone. The biosynthetic pathway is evidenced by conversion of (^{2}H)nerolidol in *Hoya purpureo-fusca, Magnolia liliiflora nigra, Robinia pseudoacacia,* and *Philadelphus coronarius.*

1. Introduction. – The two homoterpenes **1** and **2** have long been overlooked but are nonetheless widespread constituents of flower fragrances. Up to now, both compounds have been found in *ca.* 20 different flavour sources. Among them are some of the very important perfume plants like *e.g. Rosa damascena* or *Rosa centifolia* where they do occur on a trace level [1].



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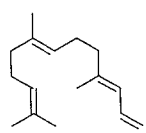
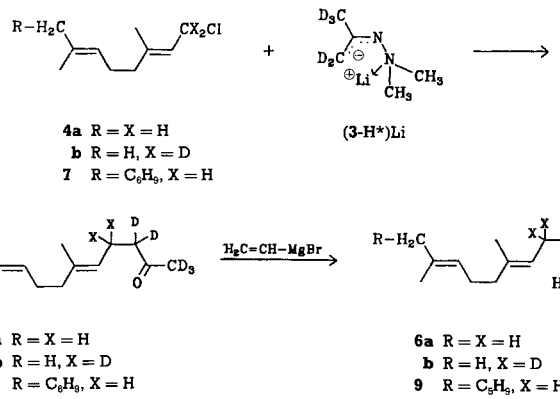


2

Although **1** and **2** have already been synthesized some 20 years ago [2], they were first recognized as natural products in 1986 by *Maurer et al.* as minor constituents of the Cardamom oil [3]. Recently, it was shown by *Kaiser* that both homoterpenes are even major constituents of the volatiles emitted from *Magnolia liliiflora* (Magnoliaceae), *Hoya carnosa* (Asclepiadaceae), *Robinia pseudoacacia* (Leguminosae), from Cactaceae like *Selenicereus hamatus* ('Queen of the night') or orchidaceae like *Aerangis friesiorum* [4]. Due to their widespread occurrence and their very recently discovered function as mediators in insect-plant interactions [5], the biosynthesis of these homoterpenes is of particular interest. According to a tentative biosynthetic scheme proposed by *Kaiser*, **1** and **2** could originate from the two regular terpene alcohols nerolidol and geranyllinalool by oxidative fragmentation into the homoterpene and but-3-en-2-one [4] (see below, *Scheme 3*).

We now report the synthesis of appropriately labelled precursors, namely (^{2}H)nerolidol and (^{2}H)geranyllinalool, and their successful administration to and metabolization by *Magnolia liliiflora nigra, Hoya purpureo-fusca, Robinia pseudoacacia,* and *Philadelphus coronarius.*

Scheme 1



4a R = X = H
b R = H, X = D
7 R = C_9H_9, X = H

(3-H*)Li

5a R = X = H
b R = H, X = D
8 R = C_9H_9, X = H

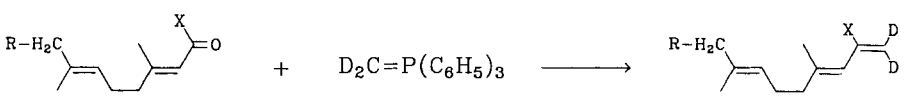
6a R = X = H
b R = H, X = D
9 R = C_9H_9, X = H

2. Synthesis of ^{2}H-Labelled Precursors. – In order to verify the proposed fragmentation [4], most promising seemed to us a ^{2}H-label at C(4) and in the Me group at C(3) of nerolidol, since thus the label should be present in each of the two fragments after biosynthetic conversion.

The required ($^2H_5$)nerolidol is readily accessible following the synthetic protocol of *Scheme 1*. Condensation of ($^2H_6$)acetone with *N,N*-dimethylhydrazine in the presence of a catalytic amount of ($^2H_4$)acetic acid and powdered molecular sieve yields the ($^2H_6$)dimethylhydrazone **3** (92% ^{2}H). If acidic ^{1}H-catalysts (*e.g.* CF_3COOH) are used, significant H/D-exchange occurs (*ca.* 70% ^{2}H). Metallation (BuLi) and subsequent alkylation of **3** with geranyl chloride (**4a**) yields geranyl($^2H_5$)acetone **5a** (> 92% ^{2}H). Addition of vinylmagnesium bromide, finally, converts **5a** into racemic ($^2H_5$)nerolidol **6a**. Complete labelling at C(5) and C(4) is achieved, if (1,1-$^2H_2$)geranyl chloride (**4b**) [7] [8] is used for alkylation of **3** (→**5b**→**6b**). Following the same sequence, alkylation of **3** with farnesyl chloride **7** affords **8** which is converted to the geranyl($^2H_5$)linalool **9**.

The required ^{2}H-labelled reference substances **12a**,**b** and **13** are obtained by *Wittig* reaction of ($^2H_2$)methylidene(triphenyl)phosphorane with either geranial (**10a**), (1-^{2}H)geranial (**10b**), or farnesal (**11**), respectively *(Scheme 2)*.

Scheme 2



10a R = X = H
b R = H, X = D
11 R = C_9H_9, X = H

12a R = X = H
b R = H, X = D
13 R = C_9H_9, X = H

3. Results. – GLC/MS analysis of the volatiles of all four species studied (see *Chapt. 1*) clearly evidence that these plants are able to convert nerolidol into the homoterpene **1**. *Fig. 1* shows a typical chromatogram of volatiles and *Fig. 2* the MS of the labelled homoterpene (1,1-$^2H_2$)-**1** as obtained from *e.g. Magnolia liliiflora nigra* after incubation with ($^2H_5$)nerolidol **6a**.

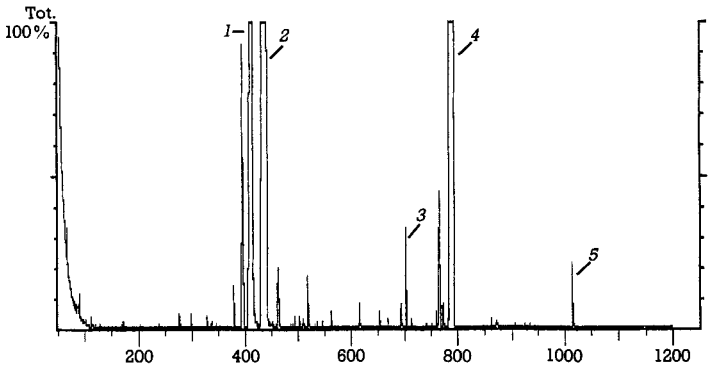


Fig. 1. *GLC analysis of volatiles of* Magnolia liliiflora nigra. Major compounds: 1 = linalool, 2 = (3*E*)-4,8-dimethylnona-1,3,7-triene (**1**), 3 = tetradecane, 4 = pentadecane, 5 = farnesol. The (^{2}H)homoterpene (^{2}H)-**1** elutes within the first front of the natural homoterpene.

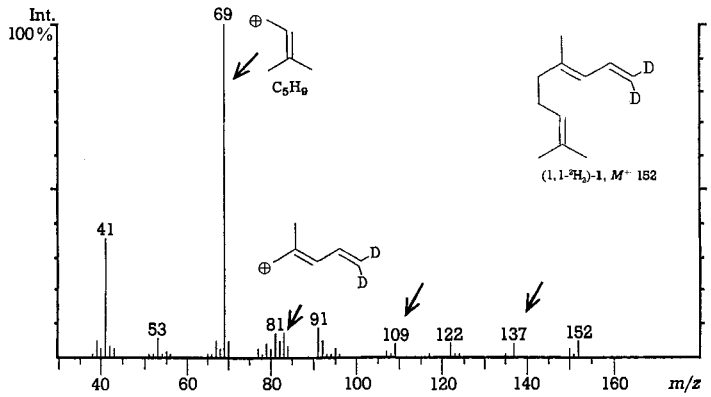


Fig. 2. *MS of (1,1-$^2H_2$)-***1** *obtained after incubation of* Magnolia liliiflora nigra *with (*$^2H_5$*)nerolidol* **6a**. Due to insufficient separation of the (^{1}H)- and the (^{2}H)compound, some fragments of the natural (^{1}H)homoterpene **1** are also present. Typical fragments of the (^{2}H)compound (1,1,-$^2H_2$)-**1** are indicated by arrows.

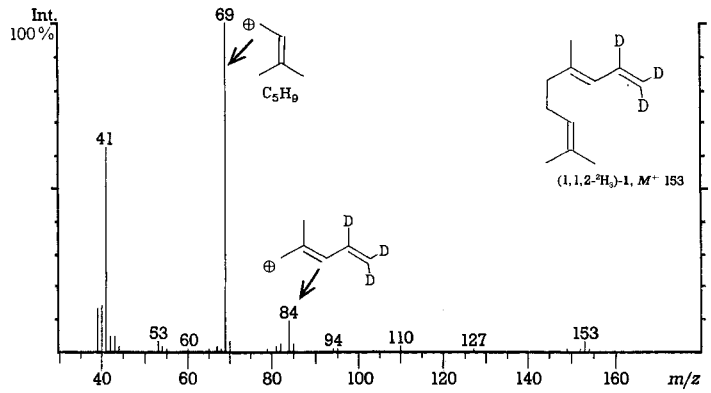


Fig. 3. *MS of (1,1,2-$^2H_3$)-***1** *obtained after incubation of* Magnolia liliiflora nigra *with (*$^2H_7$*)nerolidol* **6b**. The spectrum is fully consistent with the synthetic reference **12b** (no contamination with the natural (^{1}H)homoterpene **1**).

The molecular ion of (1,1-$^2H_2$)-**1** at *m/z* 152 (150 for **1**), together with the 2-methylpentadienyl ion at *m/z* 83 (81 for **1**) and the dimethylallyl fragment at *m/z* 69 (69 for **1**) unequivocally verify the administered ($^2H_5$)nerolidol **6a** as the precursor of the new metabolite. Furthermore, GLC and MS data are fully consistent with those of the synthetic reference **12a**.

If ($^2H_7$)nerolidol **6b** is administered to *Magnolia liliiflora nigra,* the molecular ion of the resulting ($^2H_3$)homoterpene (1,1,2-$^2H_3$)-**1** at *m/z* 153 indicates that one and only one of the originally two ^{2}H-labels at C(5) of **6b** has been lost during double-bond formation (see *Fig. 3*). Also the 2-methylpentadienyl fragment shows the expected shift to *m/z* 84, while the terminal dimethylallyl fragment remains unchanged (*m/z* 69), as is the case for the reference compound **12b**.

It is interesting to note, that the used specimens of *Philadelphus coronarius* and *Robinia pseudoacacia* do *not* produce the natural (^{1}H)homoterpenes [4], at least not at a level which can be monitored by GLC or GLC/MS. However, the required enzyme(s) have to be present, since both plants produce the ($^2H_2$)homoterpene (1,1-$^2H_2$)-**1** after administration of ($^2H_5$)nerolidol **6a**.

The second fragment, namely but-3-en-2-one, is not observed in any of the above incubation experiments. Due to its high chemical activity in addition reactions ([4 + 2] cycloaddition [6] and [1,4]addition), it might be trapped in further reactions prior to analysis.

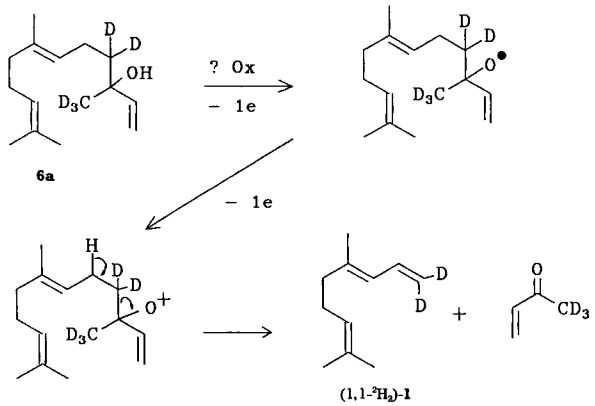
Incubation experiments with geranyl($^2H_5$)linalool **9** are as yet less conclusive. Only with *Philadelphus coronarius* and **9** the formation of a labelled (H_2)-**2** seems to occur. However, due to its very low abundance, no conclusive information about the molecular ion can be obtained. Although most of the typical fragments of the ($^2H_2$)reference **13** at *m/z* 69, 81/83, 97, and 136 *versus m/z* 69, 81, 95, 134 for the (^{1}H)compound are matched by the metabolite, further experiments with improved administration and recovery techniques are required to confirm that the same fragmentative degradation is also valid for the formation of **2** from the higher homologue geranyllinalool.

4. Discussion. – The present work provides the first experimental evidence for the biosynthesis of the homoterpenes **1** and, with restrictions, **2** from the regular terpene alcohols nerolidol or geranyllinalool, respectively. It is in agreement with the tentative biosynthetic scheme proposed by *Kaiser* [4] (see *Scheme 3*). According to this, nerolidol or geranyllinalool are enzymatically attacked at the O-atom and after electron transfer cleavage into the corresponding homoterpenes **1** or **2**, respectively, and butenone occurs.

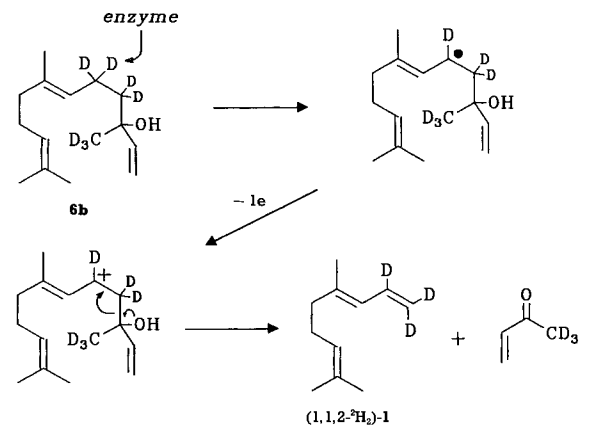
Alternatively, the enzymatic attack could also occur on C(5), leaving a radical at this position which, after a second electron transfer, could fragment into the same products (*Scheme 4*). Both mechanisms are framed by the experimental results and can as yet not be distuinguished by the hitherto performed incubation experiments.

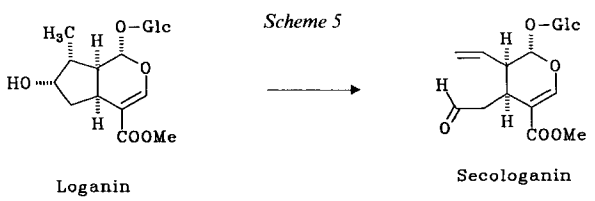
The new fragmentation of nerolidol or geranyllinalool exhibits striking similarities to the bioconversion of loganin into secologanin [10] (*Scheme 5*). In this example of a secondary alicyclic alcohol, a central σ bond between a Me group and an adjacent OH moiety is enzymatically cleaved and leads to a vinyl and aldehyde fragment within the same molecule. Intermediates which could provide evidence for the enzymatic attack at either the O-atom or the exocyclic Me group have not been observed as yet.

Scheme 3. *Biosynthesis of the Homoterpenes* **1** *or* **2** *According to* Kaiser [4], *Exemplified with* ($^2H_5$)*Nerolidol* **6a**



Scheme 4. *Biosynthesis of Homoterpenes* **1** *or* **2**. *Exemplified with* ($^2H_7$)*Nerolidol* **6b**





In the present case, determination of $K_{H/D}$ for removal of an H-atom from C(5) is expected to give more information about this principal question, and it is the subject of further investigations.

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Experimental Part

General. Solvents and reagents were purified and dried prior to use. Anh. $MgSO_4$ was used for drying operations. Solns. were generally concentrated by flash evaporation under reduced pressure. Anal. GLC: *Carlo Erba* gas chromatograph, series *4200*, equipped with fused-silica capillaries, *SE 30* (40 m × 0.31 mm); carrier gas, H_2 at 30 cm/s. IR (cm^{-1}): *Beckmann Acculab 8*. ^{1}H-NMR (250 MHz, TMS as internal standard): *Bruker Cryospec WM 250*. MS (*m/z*): *Finigan 4510* GLC/MS system and *Finnigan ITD* combined with a *Carlo Erba* gas chromatograph, model *Vega*; carrier gas, He at 30 cm/s.

(1,1,1,3,3,3-$^2H_6$)Acetone N,N-*Dimethylhydrazone* (**3**). To a well stirred soln. of ($^2H_6$)acetone (10.0 g, 0.16 mol) in CH_2Cl_2 (100 ml) were added dry, finely grounded molecular sieves (3 Å; 10.0 g) and ($^2H_4$)acetic acid (1 ml). After a brief exothermic reaction, stirring was continued for 2 h, the solids were removed by suction, the filtrate was washed with Na_2CO_3 soln. (10%) and dried (NaOH pellets), and most of the solvent was evaporated. Distillation gave 5.4 g (36%) of **3** as a colorless liquid. B.p. 93°/760 Torr. IR: 3000*s*, 2950*s*, 2860*s*, 2825*s*, 2780*m*, 2210*w*, 1635*s*, 1470*s*, 1450*m*, 1265*m*, 1020*s*, 985*m*, 725*w*. ^{1}H-NMR: 1.92 (*m*, *ca.* 0.8 H, CH_3, corresponding to *ca.* 92% ^{2}H); 2.44 (*s*, $(CH_3)_2N$). MS: 106 (100, M^+, $C_5{}^1H_6{}^2H_6N_2$), 105 (22), 104 (10), 62 (8), 61 (15), 60 (14), 58 (2), 48 (4), 47 (13), 46 (61), 45 (32), 44 (63), 43 (9), 42 (36), 40 (5).

1-Chloro-3,7-dimethyl(1,1-$^2H_2$)octa-2,6-diene (**4b**). According to [7], **4b** was prepared in 71% yield from (1,1-$^2H_2$)geraniol [6]. IR: 2980*s*, 2940*s*, 2870*s*, 2180*w*, 1660*w*, 1600*w*, 1450*m*, 1385*s*, 1195*m*, 1180*s*, 950*m*, 820*m*. ^{1}H-NMR: 1.60 (*s*, CH_3); 1.68 (*s*, CH_3); 1.72 (*d*, *J* = 2, CH_3); 2.08 (br. *m*, 2 CH_2); 5.08 (br. *t*, =CH); 5.43 (*s*, =C*H*C^{2}H$_2$); no *d* at 4.10 (CH_2Cl) indicates ≫ 98% ^{2}H. MS: 174, 176 (1, 0.5, M^+, $C_{10}H_{17}{}^2H_2Cl$); 159 (1), 139 (4), 131 (11), 123 (8), 109 (9), 97 (4), 95 (6), 82 (7), 70 (23), 69 (100), 55 (9), 53 (11), 43 (12), 41 (75).

(2H)Geranylacetone **5** *and Farnesyl(2H)acetone* **8**: *General Procedure.* To a soln. of **3** (4.4 g, 0.041 mol) in dry THF (40 ml) at −5°, BuLi (1.0 equiv.) in hexane was slowly added with stirring. The soln. turned dark. After 30 min, a soln. of the corresponding geranyl or farnesyl choride (0.041 mol) in the same solvent (50 ml) was added, and stirring was continued for 4 h. Following hydrolysis with 2N HCl (20 min) and workup (Na_2CO_3 soln., brine, H_2O), the crude products were purified by CC on silica gel (pentane/Et_2O 4:1).

6,10-Dimethyl(1,1,1,3,3-$^2H_5$)undeca-5,9-dien-2-one (**5a**). From **4a** and **3** in 64% yield. IR: 2970*s*, 2920*s*, 2860*s*, 2180*w*, 1713*s*, 1445*m*, 1380*m*, 1250*m*, 1110*m*, 1035*m*, 830*w*. ^{1}H-NMR: 1.62 (*s*, CH_3); 1.64 (*s*, CH_3); 1.69 (*s*, CH_3); 1.93–2.17 (*m*, 2 CH_2); 2.28 (*d*, *J* = 8, $CH_2C^2H_2$); 2.43 (*m*, *ca.* 0.4 H, CH_2, corresponding to ≈ 92% ^{2}H); 5.07 (*t*, *J* = 8, 2 CH=). MS: 198 (0.5, M^+, $C_{13}H_{17}{}^2H_5O$), 180 (5), 155 (5), 136 (12), 121 (4), 109 (8), 93 (8), 82 (3), 69 (68), 53 (8), 46 (70), 45 (100), 44 (51), 41 (72).

6,10-Dimethyl(1,1,1,3,3,4,4-$^2H_7$)undeca-5,9-dien-2-one (**5b**). From **4b** and **3** in 23% yield. IR: 2970*s*, 2920*s*, 2860*s*, 2215*w*, 1710*s*, 1450*m*, 1380*m*, 1260*s*, 1105*m*, 1054*m*, 825*w*. ^{1}H-NMR: 1.59 (*s*, CH_3); 1.62 (*s*, CH_3); 1.68 (*s*, CH_3); 1.90–2.15 (*m*, 2 CH_2); 2.41 (*m*, *ca.* 0.2 H, CH_2, corresponding to ≈ 97% ^{2}H); 5.05 (br. *t*, 2 CH=). MS: 201 (0.5, M^+, $C_{13}H_{15}{}^2H_7O$), 158 (4), 138 (8), 123 (3), 113 (4), 95 (5), 69 (48), 46 (100), 45 (48), 41 (48).

6,10,14-Trimethyl(1,1,1,3,3-$^2H_5$)pentadeca-5,9,13-trien-2-one (**8**). From **7** and **3** in 29% yield. IR: 2970*s*, 2920*s*, 2860*s*, 1715*s*, 1450*m*, 1375*m*, 1250*m*, 1030*m*, 990*m*, 830*w*. ^{1}H-NMR: 1.62 (*s*, 2 CH_3); 1.72 (*s*, 2 CH_3); 1.95–2.17 (*m*, 4 CH_2); 2.20 (*d*, *J* = 8, $CH_2C^2H_2$); 5.08 (*m*, 3 CH=). MS: 267 (0.7, M^+, $C_{18}H_{25}{}^2H_5O$), 224 (0.5), 204 (0.6), 183 (0.9), 161 (1), 136 (21), 112 (4), 107 (4), 95 (7), 93 (11), 81 (28), 69 (100), 55 (8), 53 (8), 46 (95), 45 (42), 41 (63).

(2H)Nerolidol **6** *and Geranyl(2H)linalool* **9**: *General Procedure.* To a chilled soln. of vinylmagnesium bromide (5.5 mmol) in dry THF (5.0 ml) were added, with stirring, **5** or **8** (5.0 mmol) in THF (5 ml). After 1 h, the mixture was hydrolyzed with sat. NH_4Cl soln., extracted with Et_2O, washed with H_2O, dried, and purified by CC on silica gel (pentane/Et_2O 9:1).

*3,7,11-(3-*methyl-$^2H_3$*)-Trimethyl(4,4-$^2H_2$)dodeca-1,6,10-trien-3-ol* (**6a**). From **5a** in 53% yield. IR: 3420 (br.), 3090*w*, 2970*s*, 2930*s*, 2860*s*, 2230*w*, 1450*m*, 1375*m*, 1110*m*, 995*m*, 920*m*, 830*m*. ^{1}H-NMR: 1.58 (*s*, 2 CH_3); 1.68 (*s*, CH_3); 1.90–2.12 (*m*, 3 CH_2); 5.05 (*dd*, *J* = 10.4, 1, 1 H, =CH_2); 5.12 (*t*, *J* = 7, 2 CH=); 5.20 (*dd*, *J* = 17.1, 1, 1 H, =CH_2); 5.92 (*dd*, *J* = 17.1, 10.4, C*H*=CH_2). MS: 209 (2, $M^+ - H_2O$, $C_{15}H_{21}{}^2H_5O$), 165 (9), 152 (3), 136 (12), 123 (31), 109 (18), 97 (34), 93 (40), 81 (31), 69 (100), 67 (39), 55 (28), 53 (30).

*3,7,11-(3-*methyl-$^2H_3$*)-Trimethyl(4,4,5,5-$^2H_4$)dodeca-1,6,10-trien-3-ol* (**6b**). From **5b** in 98% yield. IR: 3405 (br.), 3090*w*, 2970*s*, 2920*s*, 2860*s*, 2230*m*, 1640*m*, 1450*m*, 1377*s*, 1190*m*, 1105*m*, 1070*m*, 995*s*, 920*s*, 825*w*. ^{1}H-NMR: 1.60 (*s*, 2 CH_3); 1.68 (*s*, CH_3); 1.90–2.15 (*m*, 2 CH_2); 5.05 (*dd*, *J* = 10.4, 1 H, =CH_2); 5.12 (*s*, C*H*C^{2}H$_2$); 5.12 (*t*, =C*H*CH_2); 5.20 (*dd*, *J* = 17.1, 1, 1 H, =CH_2); 5.92 (*dd*, *J* = 17.1, 10.4, C*H*=CH_2). MS: 211 (5, $M^+ - H_2O$, $C_{15}H_{19}{}^2H_7O$), 138 (18), 123 (12), 111 (7), 99 (8), 95 (14), 82 (11), 74 (25), 69 (100), 55 (15), 46 (38), 41 (95).

*3,7,11,15-(3-*methyl-$^2H_3$*)-Tetramethyl(4,4-*$^2H_2$*)hexadeca-1,6,10,14-tetraen-3-ol* (**9**). From **8** in 95% yield. IR: 3410 (br.), 3090*w*, 2970*s*, 2920*s*, 2860*s*, 2230*w*, 1450*s*, 1380*s*, 1190*m*, 1110*m*, 1050*m*, 995*m*, 920*s*, 830*m*, 790*m*. ^{1}H-NMR: 1.60 (*s*, 2 CH_3); 1.68 (*s*, 2 CH_3); 1.90–2.15 (*m*, 5 CH_2); 5.05 (*dd*, *J* = 11, 1, 1 H, =CH_2); 5.05–5.15 (*m*, 3=CH); 5.20 (*dd*, *J* = 17.5, 1, 1 H, =CH_2); 5.92 (*dd*, *J* = 17.5, 1, C*H*=CH_2). MS: 277 (0.3, $M^+ - H_2O$, $C_{20}H_{29}{}^2H_5O$), 204 (1), 189 (1), 166 (1.5), 136 (5), 121 (4), 109 (8), 95 (11), 93 (10), 81 (32), 74 (12), 69 (100), 55 (12), 46 (17), 43 (15), 41 (55).

Reference Substances **12a**, **12b**, *and* **13**: *General Procedure*. To a chilled soln. of ($^2H_2$)methylidene(triphenyl)phosphorane (13.0 mmol) in dry THF (15 ml) was added, with stirring, a soln. of geranial, (1-^{2}H)geranial, or farnesal (10 mmol in 5 ml of THF). Stirring was continued for 1 h, and after usual workup, the product was purified by CC on silica gel using pentane.

4,8-Dimethyl(1,1-$^2H_2$*)nona-1,3,7-triene* (**12a**). From geranial in 50% yield. IR: 3025*w*, 2970*s*, 2930*s*, 2860*s*, 2215*w*, 1650*w*, 1450*m*, 1380*m*, 1105*m*, 975*m*, 933*m*, 880*m*, 715*m*. ^{1}H-NMR: 1.61 (*s*, CH_3); 1.69 (*s*, CH_3); 1.77 (*s*, CH_3); 2.00–2.20 (*m*, 2 CH_2); 5.1 (*m*, =CH); 5.87 (*d*, *J* = 11.3, =C*H*–CH=C^2H_2); 6.56 (*d*, *J* = 11, C*H*=C^2H_2). MS: 152 (7, M^+, $C_{11}H_{16}{}^2H_2$), 137 (7), 124 (2), 109 (9), 95 (3), 83 (17), 69 (100), 53 (6), 41 (22).

4,8-Dimethyl(1,1,2-$^2H_3$*)nona-1,3,7-triene* (**12b**). From (1-^{2}H)geranial in 71% yield. IR: 3040*m*, 2970*s*, 2930*s*, 2860*s*, 2210*w*, 1655*m*, 1540*w*, 1445*m*, 1380*m*, 1105*m*, 1020*m*, 880*m*, 825*m*, 700*s*. ^{1}H-NMR: 1.62 (*s*, CH_3); 1.68 (*s*, CH_3); 1.78 (*s*, CH_3); 2.00–2.20 (*m*, 2 CH_2); 5.10 (*m*, =CH); 5.87 (*s*, =C*H*–C^2H=C^2H_2). MS: 153 (2, M^+, $C_{11}H_{15}{}^2H_3$), 138 (2), 110 (2), 96 (1), 84 (11), 69 (100), 55 (3), 53 (3), 41 (67).

4,8,12-Trimethyl(1,1-$^2H_2$*)trideca-1,3,7,11-tetraene* (**13**). From (*E*)-farnesol *via* oxidation (MnO_2) to farnesal and *Wittig* reaction in 65% yield. IR: 3020*w*, 2960*s*, 2920*s*, 2850*s*, 2360*w*, 2210*w*, 1640*w*, 1445*m*, 1375*m*, 1100*w*, 925*m*, 825*m*, 705*s*. ^{1}H-NMR: 1.62 (*s*, 2 CH_3); 1.68 (*s*, CH_3); 1.78 (*s*, CH_3); 1.90–2.25 (*m*, 4 CH_2); 5.10 (*m*, 2 CH=); 5.84 (*d*, *J* = 11.5, =C*H*CH=C^2H_2); 6.55 (*d*, *J* = 11, C*H*=C^2H_2). MS: 205 (3, $M^+ - 15$, $C_{16}H_{24}{}^2H_2$), 177 (4), 162 (2), 136 (3), 134 (3), 121 (3), 109 (4), 95 (18), 83 (11), 81 (58), 69 (100), 67 (18), 55 (8), 53 (13), 41 (73).

Incubation Experiments. Suspensions of labelled nerolidol or geranyllinalool in H_2O (0.1–1.0 mg/ml) were sonicated (130 W) for 2 min. Freshly disconnected flower heads of *Hoya purpureo-fusca*, *Magnolia liliiflora nigra*, *Robinia pseudoacacia*, and *Philadelphus coronarius* were immersed into the emulsions of the precursors **6a**, **6b**, or **9**. After 24 h, the incubated plants were placed into fresh H_2O, and the emitted volatiles were entrapped on a charcoal filter for another 24 h as described in [9]. Following desorbtion of the filters with 2 × 15 µl CH_2Cl_2, the extracts were directly analyzed by GLC/MS.

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