

Narcissus trevithian and Narcissus geranium: Analysis and Synthesis of Compounds

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The essential oils of two narcissus varieties, *Narcissus trevithian* and *Narcissus geranium*, obtained by extraction of flowers followed by high vacuum distillation of the absolute, were analyzed by GC/MS. After separation in fractions, unknown compounds were isolated by preparative GLC and their structures established by NMR/IR spectroscopy. The synthesis of a number of new compounds, found for the first time in narcissus oil, is described. The two narcissus species are compared with respect to their main components and odor quality. All compounds found so far in narcissus varieties are listed.

INTRODUCTION

The odor of narcissus flowers is highly valued in the fragrance industry. We therefore decided to look for those varieties that had the most interesting odor. Many kinds of bulbous plants are grown in Holland, offering us the unique opportunity to make a choice from a great number of narcissus varieties. This also allowed the comparison of the odor quality of the undiluted absolute of narcissus varieties with commercial samples. From the large number of narcissus plant varieties available, 12 odorous species were collected, and a panel of perfumers selected the species *trevithian* and *geranium* as having the most interesting odor. These two types varied not only in odor character but also in their origin, as can be seen from Figure 1.

N. trevithian is a jonquil-type narcissus; the floral spikes bear three to five small golden yellow flowers with a dark yellow corolla.

N. geranium is a descendant of the Poetaz hybrids, clearly showing that *N. tazetta* and *N. poeticus* are its ancestors; the floral scape bears several fairly small creamy white flowers with yellow red-edged corolla. This is the first report of the analysis of *N. trevithian* and *N. geranium*.

Survey of Recent Literature. Several research groups have studied the chemical composition of narcissus extracts of different origin (Sakai et al., 1961; Shikiev et al., 1972; Anonis, 1983; Lamparski, 1987; Sakai, 1979; Joulain, 1985; Loo and Richard, 1986; Ehret et al., 1989). In 1989 Ehret et al. added 81 new trace components to the already known 192 compounds published by Loo and Richard (1986) and Sakai (1979). These results are summarized in Table II and compared with our findings.

ISOLATION OF ESSENTIAL OILS

Solvent Purification. Diethyl ether and methylene chloride were redistilled before use. Methanol p.a. was purified by eluting over a glass tube filled with norit, which was preconditioned for 4 h in a nitrogen stream at 150 °C, followed by redistillation.

Extraction. For practical reasons, the scapes with flowers were cut at about 6:00 a.m. and worked up as soon as possible. About 30 kg of *N. trevithian* and 23 kg of *N. geranium* flowers were processed (corresponding to 35 000 and 27 000 flowers, respectively).

To exclude isolation of any compound from green plant parts, each flower was cut from the ovary by hand and extracted immediately afterward by immersing these into

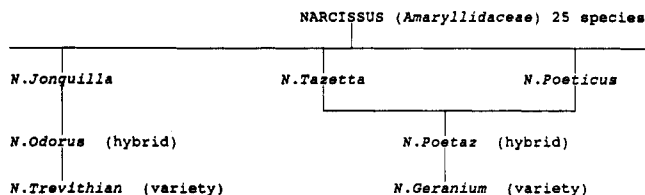


Figure 1. Narcissus varieties *N. trevithian* and *N. geranium* with respect to their genetic origin.

a mixture of methylene chloride/diethyl ether (70/30). After pressing, the extract was separated from the aqueous layer formed and dried over magnesium sulfate. The extracts (35 L) were concentrated by distillation over a 100-cm packed column at atmospheric pressure to a volume of 500 mL (concrete).

The concrete was dissolved in 600 mL of purified methanol at room temperature and the mixture cooled in CO₂/acetone to -80 °C. The waxy material was filtered through a Büchner funnel with cooling jacket and dissolved again in methanol, cooled, and separated. In total, 850 mL of methanol was used (washings included). The combined clear filtrates were now diluted with 4.2 L of water to a methanol concentration of 17% and extracted continuously with about 1.5 L of methylene chloride/diethyl ether (70/30) for 4 days. After separation and drying over magnesium sulfate, the solvents were distilled off at atmospheric pressure using a water bath to prevent overheating. Most of the residual solvent was removed by flushing with a nitrogen stream. This resulted in 16.8 g of oily material for *N. trevithian* and 8.8 g for *N. geranium*. To separate the essential oil from the high-boiling residue, molecular distillation at 10⁻⁶ mmHg and <80 °C was performed, resulting in 2.2 g of light yellow *N. trevithian* oil and 2.1 g of *N. geranium* oil. Both oils were stored before use under nitrogen at -25 °C. The odor character of the oils was judged by perfumers to be the same as that of the flowers.

Separation and Analysis. Figure 2 depicts the analytical procedure which was applied. Of both oils, 1.7 g was used for polarity separation. A glass tube (length 100 cm, diameter 2.5 cm) with Teflon tap was charged with 100 g of silica 80-100 mesh in diethyl ether. Effective column length was 45 cm. First the silica was eluted with 500 mL of pentane; subsequently, one of the narcissus oils was chromatographed using a gradient elution starting with pentane via diethyl ether to methanol. In this manner, both oils were separated into 14 fractions of 100 mL each. After drying over magnesium sulfate and

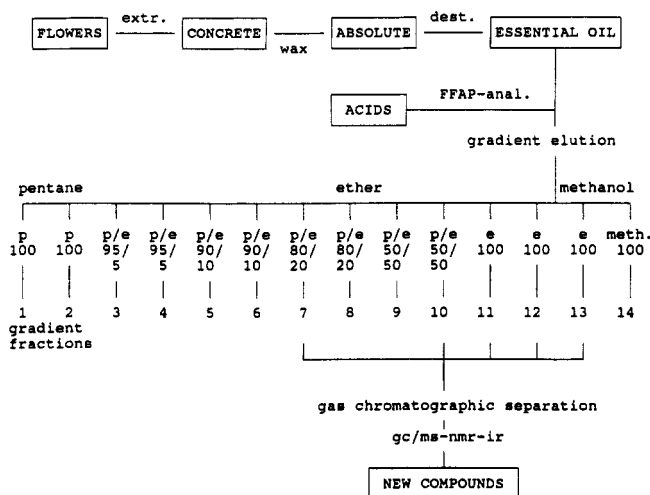


Figure 2. Schematic overview of essential oil preparation from the flowers and methods of separation into polar fractions and analysis.

removal of solvent (Rotavapor, <30 °C and 50 mmHg), each fraction was subjected to GC/MS and odor assessment. Compounds of odor interest were isolated by preparative pre-separation over a packed column followed by preparative separation of the single components on a GC equipped with a fused silica capillary. The compounds isolated were further analyzed by NMR and IR spectroscopy.

Because many acids gave broad and tailing peaks by chromatography on SE-54, both oils were also chromatographed on a FFAP column. The results were compared with the data from authentic samples.

Apparatus used were as follows: mass spectrometer, Varianmat CH 7A; NMR spectrometer, JEOL 100-MHz Type FX-100; IR spectrometer, Perkin-Elmer Models 457 (cm⁻¹) and 137E (micrometer); HPLC, Waters Millipore Type 510; gas chromatograph, Carlo Erba Type HCRG 5300; GC column (packed), 2-m diethyleneglycol succinate 10% on silica; GC column (anal.), 50-m fused silica SE-54 CL capillary; GC column (acids), 10-m fused silica FFAP capillary.

SYNTHESIS OF COMPOUNDS ISOLATED

The odor character and strength of a number of components found in *N. trevithian* were not known; therefore, synthetic samples were prepared of the compounds given below. The synthetic routes are shown schematically in Figures 3 and 4.

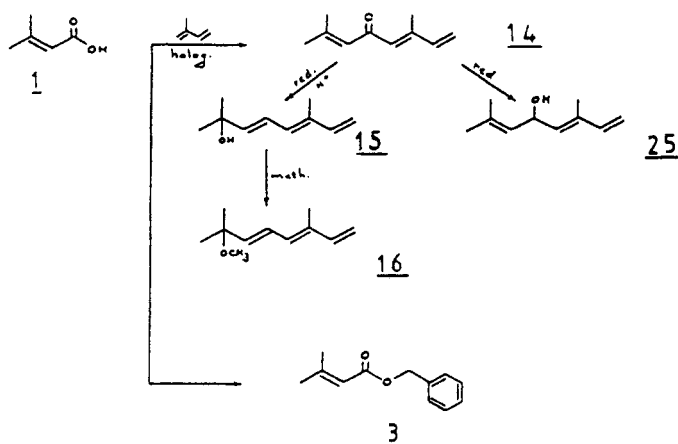


Figure 3. Schematic overview of the synthesized compounds, demonstrating the mutual relationship of these narcissus aroma components.

Benzyl 3,3-Dimethylacrylate (3). The synthesis of this ester, which was isolated from *Chamaecyparis nootkatensis* by Cheng and v. Rudloff (1970), is described inter alia by Lhommet et al. (1980).

Odor description: fresh, fatty, woody, floral, herbaceous.

2,6-Dimethyl-6-hydroxy-2,7-octadienal (11). This is the first time that this aldehyde has been found as an essential oil component. Its formation is described by Naegeli and Weber (1970), and it is patented by Ohno and Hosoi (1974). We synthesized this compound in seven steps from readily available starting materials.

Odor description: green, herbaceous, fresh, metallic, woody.

2,6-Dimethyl-2,7-octadiene-1,6-diol (12). This diol has been identified in several essential oils: *Chamaecyparis obtusa* (Matsubara et al., 1990); *Vitis vinifera* (muscat grape skins) (Strauss et al., 1988; di Stefano, 1989); *Pluchea indica* (Uchiyama et al., 1989); *Passiflora mollissima* (Forenlich et al., 1989); *Salvia sclarea* (Mazza, 1989); *Carica papaya* (Schreier and Winterhalter, 1986); and *Nicotiana tabacum* (Greek tobacco) (Behr et al., 1978). Its synthesis is described by Vig et al. (1979), and there is a Japanese patent from Hasegawa (1983).

Odor description: fatty, green, herbaceous, woody, citronella-like.

2,6-Dimethyl-3,5,7-octatrien-2-ol (15). Found in the essential oil of the white hyacinth by Mueller (1989), its formation is described by Garbers and Schneider (1970).

Odor description: fresh, rose-like floral, metallic, fatty woody.

2-Methoxy-2,6-dimethyl-3,5,7-octatriene (16). This compound has not been found as an essential oil component so far.

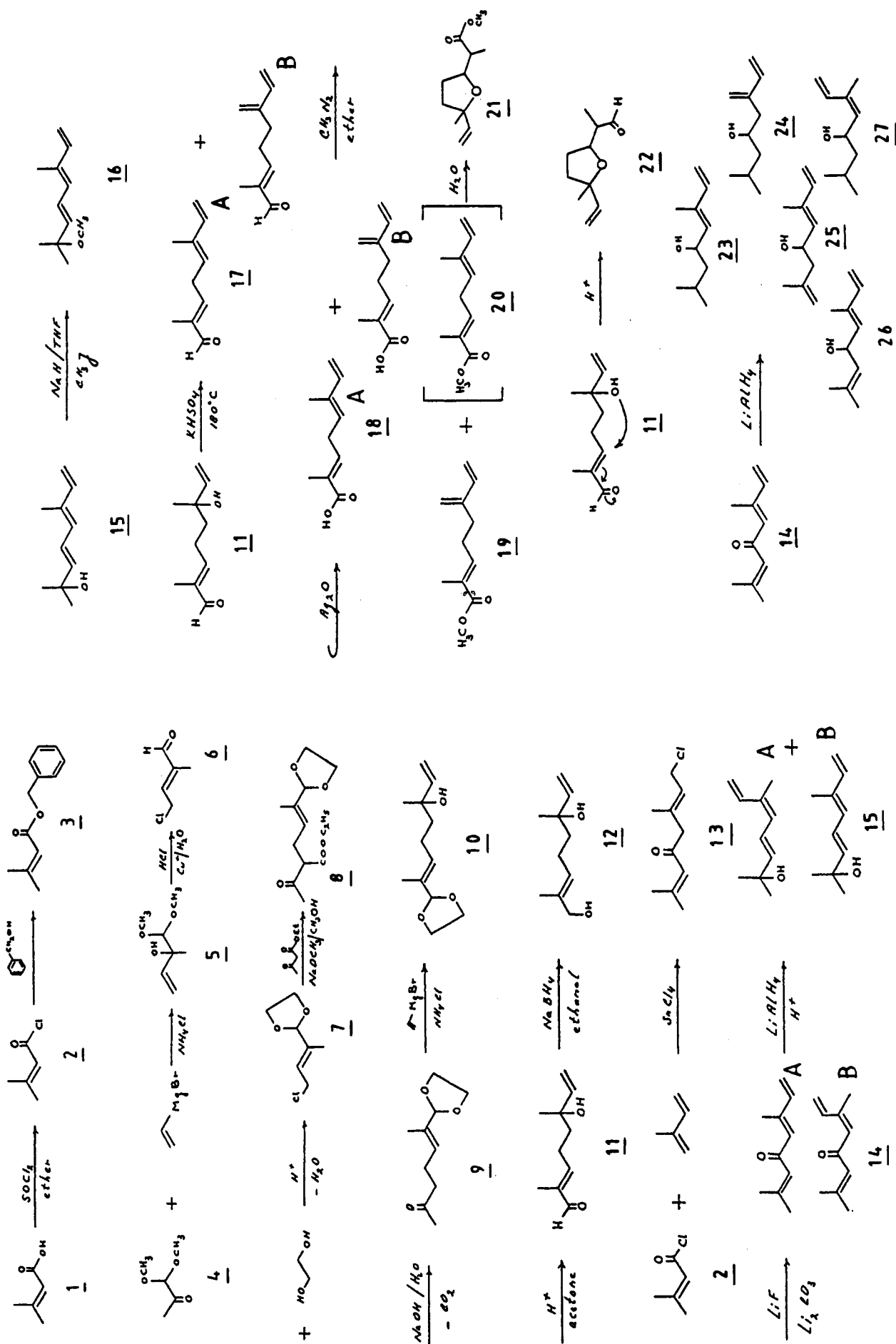
Odor description: terpenic, very fresh, fruity green, volatile.

Methyl 2,6-Dimethyl-2,5,7-octatrienoate (20). This compound has not been described as an essential oil component. In the course of its synthesis, a mixture of the isomeric acids 18A and 18B was obtained; esterification of this mixture with diazomethane yielded only the isomeric ester 19, probably as a result of isomerization.

Methyl 2-Methyl-6-methylene-2,7-octadienoate (19). Odor description: fruity, sweet, fatty, winey, metallic.

2,6-Dimethyl-2,5,7-octatrien-4-ol (26). This is the first time that this alcohol has been found in an essential oil and that its formation, as one of the reduction compounds of ketone 14, is described.

Odor description: not available due to its instability at purification.

Figure 4. Synthesis of new compounds from *N. trevithian*.

2-Methyl-2-vinyl-5-(2-formylethyl)tetrahydrofuran (Lilac Aldehyde) (22). Apart from its presence in narcissus oil, this compound is found in many other essential oils: spring flowers (Joulain, 1985); *Melilotus officinalis* (Woerner and Schreier, 1990); karo-karoude flowers (Joulain and Laurent, 1988); *Platanthera stricta* (Patt and Rhoades, 1988); bergamot oil (Schenk and Lamparsky, 1981); *Gardenia* (Hattory et al., 1977); and lilac oil (Wakayama et al., 1973). Synthesis is described by Wakayama et al. (1973) and Thomas and Ozainne (1974).

Odor description: floral, woody, sweet, metallic.

RESULTS AND DISCUSSION

For our research we used home-made flower extracts instead of commercial products, to exclude possible unreliable results as a consequence of the use of improper starting materials (e.g., mixed botanical source adulterations).

During the extraction procedures and pre separation in fractions, much attention was paid to maintain the odor quality. Each separation method was tested with a small amount of material, and the results were evaluated by perfumers. To our surprise, simple pre separation by gradient elution on a glass column with silica gel gave much better results with respect to the typical odor profiles than preparative HPLC. A possible explanation for these findings could be the large metal surface which eluting compounds have to pass in the HPLC system, leading to loss of, e.g., phenols or minor compounds with low odor threshold such as sulfur- and nitrogen-containing heterocyclic compounds, e.g., methoxypyrazines (Buttery et al., 1969). It is well-known that such minor components can, however, be of great influence on the quality of flavors and fragrances at low concentrations.

In Table II, all of the identified compounds from *N. trevithian* and *N. geranium* are listed together and compared with data from the literature. In the oil of *N. trevithian* 103 new *Narcissus* components were identified (marked with a T) and in the *N. geranium* oil, 66 components (marked with a G). Only 20 compounds are common to both oils. This brings the total amount of reported *Narcissus* compounds to about 430.

As mentioned before, a number of the identified compounds were synthesized to confirm the structure or to establish the organoleptic properties. Figure 3 is a schematic survey of the synthesis of these compounds, of which 16, 20, and 26 are found for the first time in an essential oil. The structure of 20 could be confirmed only indirectly because of isomerization of 20 into 19. All of these compounds were prepared from only two starting materials, 1 and 11, giving a clear demonstration of the structural similarities.

The first group of compounds was synthesized from 3-methyl-2-butenic acid (1). Figure 4 shows all of the reaction steps and products involved: ketone 14 was obtained as a mixture of the *E* and *Z* isomers (14A,B) as described by Nederlof (1978). Reduction of this mixture with lithium aluminum hydride in diethyl ether afforded a complex mixture of unsaturated alcohols 23–27.

Further purification of this mixture, to obtain the pure compound 26, failed in view of its instability. Acidification of the mixture with dilute sulfuric acid produced a mixture of the isomeric trienols 15A and 15B. Apparently isomerization of the initial products occurred under the reaction conditions. The same trienols were obtained in a 30% yield, when the reaction mixture of 14 and lithium aluminum hydride was acidified directly. Further alkyl-

Table I. Relative Amounts (Percent) of Identified Compounds with Respect to Their Chemical Class

chemical class	<i>N. trevithian</i>	<i>N. geranium</i>
aliphatic hydrocarbons	1.1	0.9
aromatic hydrocarbons	<0.1	<0.1
(sesqui) terpenoids	1.6	<0.1
ethers	0.5	1.9
phenols	23.6	2.7
esters	13.1	27.2
alcohols	30.0	10.8
aldehydes	1.7	0.4
ketones	0.3	0.1
acids	25.8	5.2
lactones	0.1	0.2
nitrogen/sulfur cmpds	<0.1	2.4
unidentified	±2.2	±48.2
total	100.0	100.0

ation with sodium hydride and methyl iodide gave the methyl ether 16 as a mixture of isomers. Purification was achieved by means of column chromatography. The last compound of this group is the ester 3, which was prepared by direct esterification of the acid chloride 2 with benzyl alcohol.

The second group of compounds was synthesized from the unsaturated aldehyde 11. We prepared this aldehyde, which was found for the first time in a narcissus oil, via a seven-step synthesis from the acetal 4, as can be seen in Figure 4.

Compound 11 was dehydrated to a mixture of isomeric unsaturated aldehydes 17A and 17B by heating with a small amount of potassium hydrogen sulfate at 180 °C. The mixture obtained was oxidized further with wetted silver oxide to the acids 18A and 18B. However, when this acid mixture was methylated with diazomethane, only the ester 19 was obtained. Compound 20, which was found in narcissus oil, could not be detected, probably as a result of hydration and subsequent cyclization to compound 21, which we isolated from the reaction mixture after GC purification.

When 11 was reduced with sodium borohydride in ethanol, diol 12 was obtained after purification by column chromatography over silica gel. Surprisingly, a NMR sample of 11 in tetrachloromethane cyclized almost completely to lilac aldehyde 22 on standing for several hours at 4 °C. This latter is a well-known essential oil component. The four isomers were purified by preparative GC.

When looking at Table I, we can divide all identified compounds into 12 chemical classes, which are presented together with their relative amounts in the essential oils. Although nearly half of the essential oil of *N. geranium* consists of unidentified components, the table clearly demonstrates the principal differences between the two *Narcissus* varieties: *N. trevithian* contains more phenolic compounds and fewer esters compared to *N. geranium*; there is also a remarkable amount of nitrogen/sulfur compounds present in *N. geranium*, which is mainly caused by indole and derivatives. Such compounds are known to be very important for floral odors. The high amount of alcohols and long-chain acids in *N. trevithian* probably has more influence on the (long) lastingness of its odor, rather than on the odor quality.

The differences in chemical composition are clearly reflected in the odor profiles of both oils: *N. trevithian* oil was judged as being very strong, very phenolic, narcissus-like, and green and with woody aspects. The odor of *N. geranium* oil, on the other hand, is also very strong but only slightly phenolic in character; in addition,

it was described as sweet, very flowery, and animal-like and as having many aspects of other (spring) flowers.

As can be concluded from Table II, there is only a very limited number of components which are common to most *Narcissus* varieties: some higher *n*-alkanes; some cresols; benzyl acetate; methyl benzoate and benzyl benzoate; some terpenoids such as limonene, *p*-cymene, ocimene, linalool, terpinen-4-ol, 1,8-cineole, and α -terpineol; benzyl alcohol and phenethanol; 1-nonanal; and indole. All of these are well-known essential oil compounds, but none is characteristic for narcissus oil.

On the basis of our findings, we agree with Loo and Richard (1986) that no character impact compounds are present in *Narcissus*. There can be very large differences in odor profile as a consequence of differing chemical composition of the extract as a result of botanical variation, growing conditions, and method of essential oil winning.

EXPERIMENTAL PROCEDURES

2,6-Dimethyl-6-hydroxy-2,7-octadienal (11). 2-Hydroxy-2-methyl-3-butenal Dimethyl Acetal (5). A solution of vinyl magnesium bromide in THF was prepared from 270 g (2.4 mol) of vinyl bromide and 48 g (1 atom) of magnesium. A solution of 236 g (2 mol) of methylglyoxal dimethyl acetal in 100 mL of THF was added at 28 °C over 1 h. Cooling was necessary to maintain this temperature. After 1 h of stirring at room temperature, the mixture was poured onto ice and ammonium chloride. Solid sodium chloride was added, and the saturated solution was extracted with diethyl ether. The ether solution was dried over magnesium sulfate and concentrated in vacuum: 229 g of 5 was obtained; yield 78%.

2-Methyl-4-chloro-2-butenal (6). Hydroxyacetal (5; 229 g, 1.6 mol) in 200 mL of toluene was added over 1 h at room temperature with stirring to a mixture of 500 mL of hydrochloric acid, 120 g of sodium chloride, and 12 g of copper(I) chloride. During the addition, the temperature rose to 30 °C. After stirring for an additional 6 h at 50 °C, the reaction mixture was cooled and extracted with diethyl ether. The ether solution was neutralized with aqueous sodium carbonate, dried, concentrated, and distilled: 82 g of chloroaldehyde 6, bp 80 °C at 30 mmHg, was obtained; yield 43%.

2-Methyl-4-chloro-2-butenal Ethylene Glycol Acetal (7). A mixture of 82 g (0.7 mol) of aldehyde 6, 300 mL of cyclohexane, and 93 g (1.5 mol) of ethylene glycol was boiled with a catalytic amount of *p*-toluenesulfonic acid over 5 h. When no more reaction water separated, the mixture was cooled to room temperature, neutralized with aqueous sodium carbonate, dried, concentrated, and distilled: 61.7 g of the glycol acetal 7 was obtained; bp 80 °C at 2 mmHg; yield 54%.

2-Methyl-6-oxo-2-heptenal Glycol Acetal (9). Sodium metal 9.9 g, (0.43 atom) was dissolved in 250 mL of absolute methanol, and the solution was cooled to 4 °C under dry nitrogen. Methyl acetoacetate 56 g, (0.43 mol) was added with cooling, and the mixture was stirred for 0.5 h at room temperature. Subsequently, 61 g (0.35 mol) of chloro compound 7 was added over 1 h without cooling. After the mixture was allowed to stand overnight at room temperature, a solution of 17.2 g of sodium hydroxide in 150 mL of water was added, and the reaction mixture was stirred for another 2 h at 60 °C. The reaction mixture was cooled to room temperature and, after addition of 500 mL of water, extracted with diethyl ether. The extracts were dried, concentrated, and distilled: 39.3 g of product 9 with bp 105 °C at 2 mmHg was obtained; yield 61%.

2,6-Dimethyl-6-hydroxy-2,7-octadienal Glycol Acetal (10). A solution of vinyl magnesium bromide in THF was prepared from 35 g (0.3 mol) of vinyl bromide and 6.1 g (0.25 mol) of magnesium. Without cooling, a solution of 39 g (0.21 mol) of compound 10 in 50 mL of dry THF was added over 1 h at 20–25 °C. The reaction mixture was stirred for another 0.5 h at 30 °C and poured onto ice and ammonium chloride, saturated with sodium chloride, and extracted with diethyl ether. The solution was dried over magnesium sulfate and concentrated in vacuo: 35 g of hydroxy acetal 10, bp 105 °C at 1 mmHg was obtained; yield 78%.

2,6-Dimethyl-6-hydroxy-2,7-octadienal (11). A solution of 3 g of oxalic acid in 30 mL of water was added to a solution of 35 g (0.16 mol) of acetal 10 in 130 mL of acetone with stirring for 0.5 h at room temperature. Stirring was continued for an additional 0.5 h, and the reaction mixture was neutralized with 5 g of sodium hydrogen carbonate. The acetone was removed in vacuo, and the resultant residue was extracted with diethyl ether. The extract was dried, concentrated, and distilled: 21.3 g of aldehyde, bp 100 °C at 1 mmHg was obtained; yield 79%; MS *m/e* (%) 71 (100), 43 (79), 55 (45), 41 (35), 87 (30), 83 (23), 98 (16), 135 (3); IR (CCl₄) 3612, 2814, 2758, 2708, 1693, 1643, 993, 926 cm⁻¹; NMR (CCl₄, 100 MHz) 1.29 (3H, s), 1.6 (2H, m), 1.70 (3H, br s), 2.3 (2H, m), 2.40 (1H, OH), 5.01 (1H, dd, *J* = 10 and 2 Hz), 5.16 (1H, dd, *J* = 17 and 2 Hz), 5.84 (1H, dd, *J* = 17 and 10 Hz), 6.41 (1H, br t, *J* = 7 Hz), 9.25 (1H, s) ppm.

2,6-Dimethyl-2,7-octadiene-1,6-diol (12). A solution of 1.7 g (0.01 mol) of aldehyde 11 in 30 mL of ethanol was added to a mixture of 1.9 g (0.05 mol) of sodium borohydride and 50 mL of ethanol, over about 0.5 h with stirring. The excess sodium borohydride was neutralized by adding 10% acetic acid and 400 mL of water. After extraction with diethyl ether (three times), the combined ether layers were dried and concentrated. The residue thus obtained was purified by column chromatography over silica gel with pentane/ether (1:1) and ether 100%: MS *m/e* (%) 43 (100), 71 (77), 67 (69), 55 (49), 93 (22), 119 (15), 110 (13), 137 (10); IR (CCl₄) 3616, 1104, 998, 925 cm⁻¹; NMR (CCl₄, 100 MHz) 1.24 (3H, s), 1.5 (2H, m), 1.62 (3H, br s), 2.0 (2H, m), 3.16 (2H, OH), 3.85 (2H, br s), 4.98 (1H, dd, *J* = 10 and 2 Hz), 5.14 (1H, dd, *J* = 17 and 2 Hz), 5.32 (1H, br t, *J* = 7 Hz), 5.84 (1H, dd, *J* = 17 and 10 Hz) ppm (*E* isomer).

2,6-Dimethyl-3,5,7-octatrien-2-ol (15).

2,6-Dimethyl-2,5,7-octatrien-4-one [Ocimenone (14)]. This compound was prepared according to the methods of Adams (1974), Adams et al. (1975), and Nederlof (1978), by telomerization of seneciyl chloride with isoprene and tin tetrachloride followed by dehydrohalogenation with lithium fluoride. After purification by column chromatography, a 1:1 mixture of two isomers was obtained.

Reduction of Ocimenone. Compounds 15 and 26. A solution of 7 g (0.05 mol) of ketone 14 was added to a stirred mixture of 1.5 g (0.03 mol) of lithium aluminum hydride in 50 mL of dry diethyl ether at 5–10 °C. Stirring was continued for another 0.5 h, and the excess hydride was destroyed by adding water cautiously, followed by neutralizing with 10% dilute hydrochloric acid. The reaction mixture was extracted with diethyl ether, dried, and concentrated. The residue was purified by column chromatography. A mixture of the compounds 23–27 was obtained, of which 2,6-dimethyl-2,5,7-octatrien-4-ol (26) was present in a concentration of 5.5%. The main components, compounds 23 and 24, were present at 41% and 43.5%, respectively.

Apart from these compounds, a small amount of 2,6-dimethyl-3,5,7-octatrien-2-ol (two isomers) (15) was formed as a result of isomerization of 25 and 26. The yield of 15 could be improved to 30% when the reaction mixture was acidified with a few drops of hydrochloric acid before workup. The trienols were purified by column chromatography.

2,6-Dimethyl-3,5,7-octatrien-2-ol (15): MS *m/e* (%) M152 B 43(100), 91 (69), 119 (58), 109 (49), 79 (40), 55 (32), 134 (35), 152 (25); IR (CCl₄) 3608, 3091, 3044, 1614, 1161–1154 (br), 1135, 1119, 1103, 987, 969, 906, 898, 830 cm⁻¹; NMR (CCl₄, 100 MHz) 1.29 (6H, s), 1.84 (3H, br s), 2.6 (1H, OH), 4.8–5.2 (2H), 5.73 (1H, d, *J* = 15 Hz), 5.8–6.6 (2H), 6.28 (1H, dd, *J* = 17 and 10 Hz) ppm (*E,E* isomer); NMR (CCl₄, 100 MHz) 1.29 (6H, s), 1.84 (3H, br s), 2.6 (1H, OH), 4.8–5.2 (2H), 5.64 (1H, d, *J* = 15 Hz), 5.8–6.6 (2H), 6.86 (1H, dd, *J* = 17 and 10 Hz) ppm (*E,Z* isomer).

2,5-Dimethyl-2,5,7-octatrien-4-ol (26): MS *m/e* (%) 119 (100), 91 (94), 134 (69), 77 (42), 41 (40), 79 (33), 39 (31), 105 (29); IR (CCl₄) 3618, 3583, 1592, 992, 904 cm⁻¹; NMR (CCl₄, 100 MHz) 1.70 (6H, br s), 1.75 (3H, br s), 3.2 (1H, OH), 4.8–5.5 (5H), 6.28 (1H, dd, *J* = 17 and 10 Hz) ppm (*E* isomer); NMR (CCl₄, 100 MHz) 1.70 (6H, br s), 1.80 (3H, br s), 3.2 (1H, OH), 4.8–5.5 (5H), 6.75 (1H, dd, *J* = 17 and 10 Hz) ppm (*Z* isomer).

2-Methoxy-2,6-dimethyl-3,5,7-octatriene (16). A solution of 2.2 g (0.015 mol) of trienol 15 in 25 mL of THF was added to a stirred suspension of 0.6 g (0.02 mol) of sodium hydride in 100

Table II (Continued)

reference:	Sakai et al. (1961)	Shikiev (1972)	Sakai (1979)			Loo et al. (1986)	Ehret et al. (1989)	this paper	
<i>Narcissus</i> sp: variety:	<i>tazetta</i> <i>chinensis</i>	<i>tazetta</i> <i>florepl</i>	<i>tazetta</i> <i>chinensis</i>	<i>tazetta</i> <i>papyr</i>	<i>jonquille</i>	not specified	<i>poeticus</i>	<i>jonquille</i> <i>trevithian</i>	<i>tazet + poet</i> <i>geranium</i>
diphenyl oxide									G
dibenzofuran									G
<i>p</i> -nitroanisole									G
5,6- β -ionone epoxide									G
(<i>Z</i>)/(<i>E</i>)- <i>trans</i> -linalool oxide						+		+	+
2,6,6-trimethyl-2-vinyl-5-hydroxy- tetrahydropyran (two isomers)								T	G
2-hydroxy-1,8-epoxy- <i>p</i> -menthane									G
(<i>E</i>)-anethole								T	G
(<i>Z</i>)-anethole								T	
ethylene glycol monoethyl ether									G
<i>p</i> -hydroxybenzyl methyl ether								T	
<i>p</i> -hydroxybenzyl ethyl ether								T	
methyl vanillyl ether								T	
3,4-dimethoxystyrene								T	
2-methoxy-2,6-dimethyl- 3,5,7-octatriene								T	
chavicol methyl ether								T	
2-pentylfuran							+		
phenols									
<i>m</i> -cresol			+	+	+				+
<i>p</i> -cresol						+		+	+
butylhydroxytoluene (BHT)			+	+	+			+	
guaiacol						+		+	
4-methylguaiacol						+			
4-ethylguaiacol						+			
4-vinylguaiacol						+		+	+
4-(2-oxopropyl)guaiacol							+		
phenol						+		+	+
<i>p</i> -nitrophenol								T	G
<i>o</i> -benzylphenol									G
<i>p</i> -vinylphenol								T	G
<i>p</i> -methoxyphenol								T	
(<i>Z</i>)- <i>p</i> -propenylphenol								T	
(<i>E</i>)- <i>p</i> -propenylphenol								T	
2,6-dimethoxy-4-propenylphenol						+			
2-methoxy-4-(hydroxyethyl)phenol								T	
eugenol						+		+	+
epoxyeugenol							+		
(<i>Z</i>)-isoeugenol						+		+	+
(<i>E</i>)-isoeugenol						+	+	+	+
methyl everniate						+			
carvacrol							+		
thymol							+		
methyl β -orcine carboxylate							+		
hydroquinone								T	G
chavicol								T	
4-allylsyringol								T	
esters									
benzyl formate						+			+
2-phenylethyl formate						+			
cinnamyl formate			+	+					+
(<i>Z</i>)-3-hexenyl acetate						+	+	+	+
bornyl acetate								T	
tetradecenyl acetate								T	
benzyl acetate	+	+	+	+	+	+	+	+	+
myristyl acetate								T	
prenyl acetate									G
2-phenylethyl acetate	+		+		+	+			+
2-(<i>o</i> -methoxyphenyl)ethyl acetate			+						
2-(<i>p</i> -methoxyphenyl)ethyl acetate									G
3-phenylpropyl acetate	+		+				+		+
3-(<i>o</i> -methoxyphenyl)propyl acetate			+						
(<i>Z</i>)/(<i>E</i>)-cinnamyl acetate			+			+			+
<i>o</i> -methoxybenzyl acetate			+	+					
anisyl acetate									G
lilac acetate									G
geranyl acetate									G
nerolidyl acetate							+		
epoxylinalyl acetate							+		
hexyl acetate						+			
heptyl acetate							+		
octyl acetate						+			
benzylphenyl acetate						+	+		

Table II (Continued)

reference:	Sakai et al. (1961)	Shikiev (1972)	Sakai (1979)			Loo et al. (1986)	Ehret et al. (1989)	this paper	
<i>Narcissus</i> sp: variety:	<i>tazetta</i> <i>chinensis</i>	<i>tazetta</i> <i>florepl</i>	<i>tazetta</i> <i>chinensis</i>	<i>tazetta</i> <i>papyr</i>	<i>jonquille</i>	not specified	<i>poeticus</i>	<i>jonquille</i> <i>trevithian</i>	<i>tazet + poet</i> <i>geranium</i>
(Z)-2-hexenyl acetate						+			
linalyl acetate					+	+			
terpenyl acetate						+			
menthyl acetate			+						
phenylmethyl acetate		+							
hotrienyl acetate								T	
benzyl butyrate					+				
hexyl isobutyrate								T	
benzyl isobutyrate					+				
citronellyl isobutyrate							+		
methyl β -hydroxyvalerate								T	
2-phenylethyl isovalerate							+		
benzyl isovalerate						+			
(E)-3-hexenyl caproate							+		
benzyl tiglate						+			
benzyl 3,3-dimethylacrylate								T	G
ethyl heptanoate						+			
ethyl octanoate						+			
ethyl nonanoate						+			
methyl benzoate		+	+	+	+	+		+	+
ethyl benzoate						+			
butyl benzoate								T	
isobutyl benzoate								T	
n-amyl benzoate						+			
isoamyl benzoate						+	+	+	
isoprenyl benzoate								T	
hexyl benzoate							+	+	+
(Z)/(E)-3-hexenyl benzoate				+	+	+		+	
2-phenylethyl benzoate						+		+	+
3-phenylpropyl benzoate						+		+	+
methyl p-hydroxybenzoate								T	G
linalyl benzoate								T	
cinnamyl benzoate									G
benzyl benzoate					+	+	+	+	+
2,6-dihydroxybenzyl benzoate									G
methyl 3,4-dimethoxybenzoate								T	
benzyl 2,6-dihydroxybenzoate								T	
3-methyl-2-butenyl benzoate					+			+	+
dimethyl phthalate								T	G
diethyl phthalate								T	G
dibutyl phthalate								T	G
methyl salicylate						+		+	+
ethyl salicylate						+			
isoamyl salicylate							+		
benzyl salicylate						+		+	+
phenylethyl salicylate						+			
phenylpropyl salicylate								T	G
methyl cinnamate		+	+	+	+			+	
ethyl cinnamate							+		
benzyl cinnamate								+	
cinnamyl cinnamate							+		
methyl dihydrocinnamate							+		
ethyl dihydrocinnamate							+		
methyl o-anisate							+	+	+
methyl p-anisate							+	+	+
methyl nicotinate								T	
methyl vanillate								T	G
methyl geranate								T	
methyl veratrate					+		+		
methyl anthranilate		+	+	+	+				
methyl butylcarbaminate									G
methyl 2,6-dimethyl- 2,5,7-octatrienoate								T	
methyl phenylpropionate					+				
methyl α -phenylhydroxy- propionate								T	
methyl undecylate								T	
methyl dodecylate							+		
ethyl dodecylate						+			
methyl tridecylate								T	
methyl myristynate								T	
ethyl myristynate							+		
isopropyl myristynate								T	G
ethyl pentadecanoate						+			

Table II (Continued)

reference:	Sakai et al. (1961)	Shikiev (1972)	Sakai (1979)			Loo et al. (1986)	Ehret et al. (1989)	this paper	
<i>Narcissus</i> sp: variety:	<i>tazetta</i> <i>chinensis</i>	<i>tazetta</i> <i>florepl</i>	<i>tazetta</i> <i>chinensis</i>	<i>tazetta</i> <i>papyr</i>	<i>jonquille</i>	not specified	<i>poeticus</i>	<i>jonquille</i> <i>trevithian</i>	<i>tazet + poet</i> <i>geranium</i>
methyl palmitate							+	+	+
ethyl palmitate						+	+		
isopropyl palmitate									G
methyl palmitoleate							+		
methyl stearate							+		
ethyl stearate						+			
methyl linoleate							+	+	+
ethyl linoleate						+			
benzyl linoleate							+		
methyl linolenate							+		
ethyl linolenate						+			
benzyl linolenate							+		
ethyl oleate						+			
alcohols									
1-butanol						+			
3-methylbutanol							+		
2-methyl-3-buten-2-ol							+		
3-methyl-2-buten-1-ol			+	+				+	+
1-pentanol							+		
pentan-2-ol						+			
3-penten-1-ol								T	
3-methylpentanol						+			
1-hexanol						+		+	+
hexan-2-ol						+			
hexan-3-ol						+			
(E)-2-hexen-1-ol						+			
(Z)-3-hexen-1-ol						+		+	+
(E)-3-hexen-1-ol						+			
1-heptanol	+		+	+	+	+			+
2-hepten-1-ol						+			
heptan-3-ol							+		
2-methyl-2-hepten-6-ol								T	
6-methyl-5-hepten-2-ol							+		
1-octanol						+			
octan-3-ol						+			
1-octen-3-ol						+			
3,7-dimethyl-1,5,7-octatrien-3-ol (hotrienol)								T	G
2,6-dimethyl-1,7-octadiene-3,6-diol								T	
2,6-dimethyl-7-octene-1,6-diol								T	
2,6-dimethyl-2,7-octadiene-1,6-diol								T	
2,6-dimethyl-3,5,7-octatrien-2-ol								T	
2,6-dimethyl-2,5,7-octatrien-4-ol								T	
2-methyl-6-methylene-2,7-octadiene-2,6-diol								T	
2,6-dimethyl-3,7-octadiene-2,6-diol								T	
2,6-dimethyl-2,7-octadiene-4,6-diol (two isomers)								T	
1-nonanol							+		
1-decanol									
1-undecanol								T	
1-dodecanol						+			
1-tridecanol							+		+
tridecan-2-ol								T	
1-hexadecanol							+		+
1-octadecanol									
1-nonadecanol		+							
1-docosanol									G
3,7,11,15-tetramethyl-1,6,10,14-hexadecatetraen-3-ol								T	
3,7,11-trimethyl-1,3,6,10-dodecatetraen-8-ol								T	
benzyl alcohol	+	+	+	+	+	+	+	+	+
<i>o</i> -methoxybenzyl alcohol			+	+					
linalool	+	+	+	+	+	+		+	+
menthol			+					+	
bornel								T	
citronellol						+			
<i>p</i> -cymen-8-ol						+		+	
2-butoxyethanol						+			
perillyl alcohol						+			
cinnamyl alcohol						+	+		+
geraniol		+				+		+	
nerol		+							

Table II (Continued)

reference:	Sakai et al. (1961)	Shikiev (1972)	Sakai (1979)			Loo et al. (1986)	Ehret et al. (1989)	this paper	
<i>Narcissus</i> sp: variety:	<i>tazetta</i> <i>chinensis</i>	<i>tazetta</i> <i>florepl</i>	<i>tazetta</i> <i>chinensis</i>	<i>tazetta</i> <i>papyr</i>	<i>jonquille</i>	not specified	<i>poeticus</i>	<i>jonquille</i> <i>trevithian</i>	<i>tazet + poet</i> <i>geranium</i>
β -ionone							+		+
camphor									G
2,6,6-trimethyl- 2-hydroxycyclohexanone									G
hexadecan-2-one						+			
heptadecan-2-one						+			
6-methylhepten-2-one						+		+	
acetophenone								T	
methyl vinyl ketone								T	
tridecan-2-one						+		+	+
pentadecan-2-one						+		+	+
benzophenone								T	
acetoin								T	
maltol								T	
3-methoxy-4-(hydroxyphenyl)- propan-2-one								T	
acetovanillone								T	
cyclohexanone								T	
verbenone								T	
1,2-epoxy β -ionone							+		
6-methyl-4,6-heptadien-2-one							+		
3-octen-2-one							+		
pulegone							+		
hexan-3-one							+		
undecan-2-one							+		
dodecan-3-one							+		
6,10,14-trimethylpentadecan-2-one							+		
heptadecan-2-one						+			
<i>p</i> -methylacetophenone			+			+			
acids									
propionic acid								T	
butyric acid							+	+	
2-methylbutyric acid									G
valeric acid								T	
caproic acid						+		+	+
heptanoic acid						+		+	+
caprylic acid						+			
nonanoic acid						+		+	+
decanoic acid						+		+	+
undecanoic acid									G
dodecanoic acid							+	+	+
tridecanoic acid								T	G
tetradecanoic acid						+		+	+
pentadecanoic acid						+		+	+
palmitic acid						+		+	+
heptadecanoic acid								T	
stearic acid						+			+
linoleic acid						+		+	+
linolenic acid						+		+	+
oleic acid								T	G
arachinic acid								T	
geranic acid						+			
salicylic acid						+			
(<i>E</i>)-cinnamic acid						+			+
3-methylcrotonic acid									G
2,6-dimethyl-6-hydroxy- 2,7-octadienoic acid								T	
2,6-dimethyl-6-hydroxy- 7-octenoic acid								T	
lactones									
γ -butyrolactone									G
γ -caprolactone									G
4-methoxy-2,3-dimethyl- 2-nonen-4-olide									G
γ -dodecalactone									G
δ -octadecalactone									G
bovolide									G
dihydroactinidiolide						+			+
phthalide									G
coumarin						+	+	+	
γ -undecalactone	+		+	+					
jasmin lactone							+		
nitrogen and sulfur cmpds									
indole	+		+	+	+			+	+

Table II (Continued)

reference:	Sakai et al. (1961)	Shikiev (1972)	Sakai (1979)			Loo et al. (1986)	Ehret et al. (1989)	this paper	
<i>Narcissus</i> sp:	<i>tazetta</i>	<i>tazetta</i>	<i>tazetta</i>	<i>tazetta</i>		not		<i>jonquille</i>	<i>tazet + poet</i>
variety:	<i>chinensis</i>	<i>florepl</i>	<i>chinensis</i>	<i>papyr</i>	<i>jonquille</i>	specified	<i>poeticus</i>	<i>trevithian</i>	<i>geranium</i>
oxindole								T	G
diphenylamine								T	
phenylacetoneitrile							+		
benzothiazole									G
2-methoxy-3-isobutylpyrazine								T	
dimethyl sulfone									G
dibenzothiophene									G
mint sulfide							+		

^a T, only detected in *N. trevithian*. ^b G, only detected in *N. geranium*.

mL of THF at 50 °C. After 0.5 h of stirring, 5.7 g (0.04 mol) of methyl iodide was added, and the reaction mixture was stirred for an additional 2 h at 50 °C. After cooling, the reaction product was poured into water and extracted with diethyl ether. The extract was dried and concentrated, and after solvent evaporation, the residue was purified by column chromatography: MS *m/e* (%) M166 B119 (100), 91 (100), 43 (94), 59 (86), 77 (47), 151 (47), 134 (38), 166 (36); IR (CCl₄) 3093, 3045, 2825, 1612, 1254, 1170, 1078, 988, 972, 899, 750, 812 cm⁻¹; NMR (CCl₄, 100 MHz) 1.24 (6H, s), 1.85 (3H, br s), 3.06 (3H, s), 4.96 (1H, d, *J* = 10 Hz), 5.12 (1H, d, *J* = 17 Hz), 5.60 (1H, d, *J* = 15 Hz), 5.95 (1H, br d, *J* = 10 Hz), 6.30 (1H, dd, *J* = 17 and 10 Hz), 6.35 (1H, dd, *J* = 15 and 10 Hz) ppm (*E,E* isomer from narcissus oil and synthesis); NMR (CCl₄, 100 MHz) 1.24 (6H, s), 1.85 (3H, br s), 3.06 (3H, s), 4.9–5.3 (2H), 5.52 (1H, d, *J* = 15 Hz), 5.8–6.6 (2H), 6.84 (1H, dd, *J* = 17 and 10 Hz) ppm (*E,Z* isomer).

Methyl 2-Methyl-6-methylene-2,7-octadienoate (19) and Methyl 2,6-Dimethyl-2,5,7-octatrienoate (20) (Attempted Synthesis). 2,6-Dimethyl-2,5,7-octatrienal (17A) and 2-Methyl-6-methylene-2,7-octadienal (17B). Seventeen grams of hydroxylaldehyde 11 was dehydrated in portions by vacuum distillation over a catalytic amount of potassium hydrogen sulfate. Redistillation yielded 8.7 g of a mixture of both isomers and lilac aldehyde (22); bp 105 °C at 8 mmHg.

2,6-Dimethyl-2,5,7-octatrienoic Acid (18A) and 2-Methyl-6-methylene-2,6-octadienoic Acid (18B). Aldehyde mixture (17A,B) (1.68 g, 0.01 mol) was added to a solution of 3.4 g (0.02 mol) of silver nitrate in 50 mL of water; while stirring at 50 °C, a solution of 1.6 g (0.04 mol) of sodium hydroxide in 30 mL of water was added gradually, and stirring was continued for another 2 h. After cooling, the reaction mixture was filtered; 100 mL of diethyl ether was added to the alkaline filtrate, followed by dropwise addition of 10% hydrochloric acid till the solution was discolored. The ether layer was separated, dried, and concentrated.

Methyl 2,6-Dimethyl-2,5,7-octatrienoate (20) (Attempted Synthesis). The unpurified mixture of 18A,B was esterified with an excess of diazomethane in diethyl ether at 10 °C over 3 h. The ether solution was concentrated in vacuo, and the resulting oil was purified by column chromatography. A mixture of methyl ester 19 and the cyclized ester 21 (mixture of isomers) was obtained. Compound 20 could not be detected. Apparently, 20 is cyclized to 21.

Methyl 2-Methyl-6-methylene-2,7-octadienoate (19): MS *m/e* (%) 80 (100), 93 (99), 105 (86), 121 (78), 112 (70), 125 (55), 41 (62), 180 (37); IR (CCl₄) 1717, 1120, 1086, 988, 900 cm⁻¹; NMR (CCl₄, 100 MHz) 1.79 (3H, br s), 2.3 (4H), 3.66 (3H, s), 4.9–5.3 (4H), 6.30 (1H, dd, *J* = 17 and 10 Hz), 6.66 (1H, br t) ppm.

2-Methyl-2-vinyl-5-(2-formylethyl)tetrahydrofuran (Lilac Aldehyde) (22). The synthesis is described by Thomas and Ozainne (1974). This compound was obtained both from 11 by standing for some hours in tetrachloromethane solution (yield 70%) and as a byproduct with the dehydration of 11 over potassium hydrogen sulfate. Purification was achieved by preparative gas chromatography (four diastereoisomers).

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