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IDENTIFICATION OF A MINOR COMPONENT OF THE SEX PHEROMONE OF *Leucoptera malifoliella* (LEPIDOPTERA, LYONETIIDAE)

M. RIBA,[1] J.A. ROSELL,[1] M. EIZAGUIRRE,[1] R. CANELA,[1] and A. GUERRERO[2]

[1]*Centre R + D (UPC-IRTA)*
Av. Rovira Roure, 177. 25006, Lérida
[2]*Departamento de Química Orgánica Biológica*
C.I.D. (CSIC)
Jordi Girona Salgado, 18–26. 08034, Barcelona, Spain

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Abstract—A new minor component in the female volatile extract of *Leucoptera malifoliella* (Costa) (Lepidoptera, Lyonetiidae) has been identified as 5,9-dimethyloctadecane (**2**). The amount detected of the minor compound **2** ranged from 4 to 8% in comparison with the major component 5,9-dimethylheptadecane (**1**). Neither compound has been found in the male volatile extract. The identification has been based on its spectroscopic properties and chromatographic behavior in comparison with an authentic synthetic sample. The synthesis has been carried out through a short route from 2,6-dimethylcyclohexanone (**3**). In field tests, compound **2** appears to act as a synergist of the major component **1** when mixed with the latter in a 100:0.1–5 ratio.

Key Words—Sex pheromone, *Leucoptera malifoliella*, identification, minor component, synergism, Lepidoptera, Lyonetiidae.

INTRODUCTION

The mountain-ash bentwing *Leucoptera malifoliella* (Costa) (Lepidoptera, Lyonetiidae), formerly *Leucoptera scitella* (Zeller), is considered one of the most important pests of orchards in many temperate regions of Europe and in the Central Asia mountains (Réal, 1966). Although the larvae are polyphagous, they feed preferentially on apple and pear trees, causing severe damage on the foliaceous tissue. The number of annual generations varies with the climate and

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season. In Italy four generations per year have been reported (Briolini, 1960; Ferro, 1961), one in England (Stainton, 1950), and two in other temperate areas of Europe. In the region of Catalunya, in northeast Spain, we have recorded three to four overlapping generations.

Because of the notable crop losses induced by this leafminer, monitoring and control of the pest by pheromones appears to be an attractive target. However and only until very recently, the major component of the female sex pheromone had not been identified. The compound, 5,9-dimethylheptadecane (**1**), is the first dimethyl-substituted hydrocarbon reported as a sex pheromone of a moth species (Francke et al., 1987). In other insects, branched hydrocarbons have also been sparsely found as sex pheromones. Thus, Roelofs and Cardé (1971) reported 2-methylheptadecane as sex pheromone and attractant of several species of Arctiidae, Sugie et al. (1984) identified 14-methy-1-octadecene in the peach leafminer moth *Lyonetia clerkella,* and Francke and coworkers (1988) found 5,9-dimethylpentadecane as sex pheromone of the coffee leafminer *Leucoptera coffeella.* Reported minor components are 2-methylhexadecane, 2-methyloctadecane, and 2-methylnonadecane in *Holomelina lamae* (Schal et al., 1987) and 5,9-dimethylhexadecane both in *Leucoptera scitella* and *Perileucoptera coffeella* (Francke et al., 1988). In Diptera, Carrière et al. (1988) have identified 3,7-dimethylnonadecane as the sex pheromone of the alfalfa blotch leafminer, *Agromyza frontella,* whereas several dimethyl- and trimethyl-substituted hydrocarbons of 37–40 carbon chain length have been reported as sex pheromones of tse-tse flies (Carlson et al., 1978).

In this paper, we describe the identification of 5,9-dimethyloctadecane (**2**) as a new minor component in the female volatile secretion of *Leucoptera malifoliella,* based on its spectroscopic properties and chromatographic behavior in comparison with an authentic sample. The compound has not been found in the male volatiles. In field tests, compound **2** significantly enhances the attractant activity of the major component **1** when mixed with the latter in a 100 : 0.1–5 ratio.

METHODS AND MATERIALS

Volatile Collection. Overwintering pupae were collected from infested orchards in several areas of Lérida province. The pupae were sexed with the aid of a 40× microscope and held over humidified cardboard pieces or apple tree leaves at 28°C and 18 : 6 hr light–dark cycle until emergence. For volatile collection, 1- to 2-day-old unmated males and females were kept for 2–3 days in a 1-liter Erlenmeyer flask, through which a purified airstream was passed at a flow rate of ca. 1 ml/min. The air was purified on a Porapak Q 60–80 mesh

filter, which had been previously conditioned as already described (Cross et al., 1976). The emitted volatiles were condensed on a U-tube cooled to −78°C, which was rinsed twice a day with nanograde hexane. The extract was concentrated to a 200-μl volume under a gentle stream of nitrogen for identification.

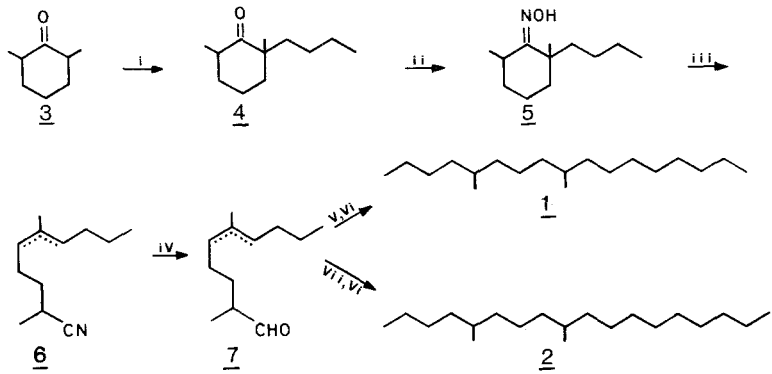
Identification. Gas chromatographic analyses were carried out on Carlo Erba Mega 5160 and 4130 models, equipped with a split–splitless dual-mode injection system, provided with a FID detector. Three fused silica capillary columns of different polarities were used: SPB-1, 25 m × 0.25 μm ID (column A); SPB-35, 15 m × 0.25 μm ID (column B); and Supelcowax-10, 30 m × 0.25 μm ID (column C). Gas chromatographic conditions were as follows: injector temperature: 250°C, detector temperature: 250°C, column temperature: isothermal at 100°C for 6 min, then programmed to 250°C at 4°C/min and held at this temperature for 15 min. Hydrogen (0.5 ml/min) was used as carrier gas.

GC-MS analyses were conducted on a HP-5995 at 70 eV in the EI mode, whereas a HP-5988A model with methane as ionizing gas was utilized in the CI mode. The high-resolution NMR spectrum of ca. 20 μg of the active material was recorded on a Varian XL-200 (200 MHz), using C_6D_6 as solvent in a 60-μl spherical microcell.

Synthesis. Boiling points were determined on a Kugelrohr distillation apparatus and are uncorrected. IR spectra were recorded in CCl_4 solution on a Perkin Elmer 399B grating spectrometer. [^{1}H]NMR spectra were determined in $CDCl_3$ solution on a Bruker WP80SY spectrometer operating at 80 MHz, and absorptions are expressed in δ scale relative to TMS. GLC analyses were performed on a Carlo Erba Vega 6000 model, equipped with a FID detector, using a 3% OV-101 glass column, 2 m × 3 mm ID, on Chromosorb W (nitrogen as carrier gas).

Reactions requiring anhydrous and oxygen-free conditions were performed under a dried inert atmosphere (N_2). Anhydrous solvents were prepared as follows: tetrahydrofuran (THF) by distillation from Na/benzophenone, hexane from Na, dimethylformamide (DMF) from CaH_2 and pyridine from KOH.

*2-n-Butyl-2,6-dimethylcyclohexanone (**4**).* This compound was prepared by a modification of the Kocienski procedure (1977) (Scheme 1). Thus, in a 250-ml, three-neck, round-bottom flask with a magnetic stirrer, reflux condenser, addition funnel, and nitrogen inlet was placed 2.16 g (45 mmol) of a 55% oil dispersion of NaH. After removing the mineral oil with pentane, 45 ml of anh. THF and 5 ml of anh. DMF were added. The mixture was heated to reflux and 4.72 g (37.5 mmol) of 2,6-dimethylcyclohexanone (**3**) was added slowly. When gas evolution had subsided, the mixture was cooled to room temperature and 5.0 g (37.5 mmol) of *n*-butyl bromide added. The reaction mixture was stirred for 1 hr at room temperature and then refluxed for 1 hr more. Then 25 ml of



i: NaH, n—C_4H_9Br/THF-DMF (30%); ii: $NH_2OH.HCl$, AcONa/EtOH (92%); iii: TsCl/pyridine (64%); iv: DIBAH/hexane (83%); v: Ph_3P^+n-$C_7H_{15}Br^-$, n-BuLi/THF (60%); vi: H_2, Pd/C (86%); vii: Ph_3P^+n—$C_8H_{17}Br^-$, n—BuLi/THF (67%).

SCHEME 1. Synthetic route to compounds **1** and **2**.

2N H_2SO_4 was added, and the reflux continued for 2 hr. After cooling to room temperature, the organic layer was decanted, and the aqueous phase was extracted with ether (3× 30 ml), washed with brine, and dried ($MgSO_4$). The solvent was stripped off, and the residue was fractionally distilled under reduced pressure to afford a mixture of 1.34 g (28%) of the starting ketone **3**, which could be recycled, and 2.06 g (42% from unreacted starting material) of the desired ketone **4**, bp 90–95°C/12 torr.

IR: ν 2920, 1700, 1455, 1375 cm^{-1}. [^{1}H]NMR: δ 0.87 (t, 3H, J = 6.5 Hz, $CH_2C\underline{H}_3$), 0.97 (s, 3H, $C\underline{H}_3CCH_2$), 0.95 (d, 3H, J = 7.5 Hz, $C\underline{H}_3CH$), 1.05–2.1 (c, 12H, $6CH_2$), 2.55 (m, 1H, CHCO). MS m/z (relative intensity): 182 (M^+, 18), 139 (7), 127 (60), 126 (100), 124 (76), 112 (11), 111 (71), 109 (30), 98 (18), 97 (45), 96 (10), 95 (61), 84 (26), 83 (24), 82 (36), 81 (15), 70 (25), 69 (56), 68 (13), 67 (14), 57 (18), 56 (51), 55 (75), 53 (11), 43 (16), 41 (43).

2-n-Butyl-2,6-dimethylcyclohexanone Oxime (5). A mixture of 1.6 g (8.8 mmol) of ketone **4**, 3.37 g (48.5 mmol) of hydroxylamine hydrochloride, 6.7 g (48.5 mmol) of sodium acetate trihydrate, and 15 ml of ethanol was refluxed for two days. After quenching with water and extracting with ether, the organic layer was washed with brine (4× 20 ml), dried ($MgSO_4$), and concentrated under vacuum. The residue was distilled to give 1.60 g (92%) of oxime **5** as a colorless oil, bp 127–135°C/10 torr.

IR: ν 3230, 2920, 1455, 1375, 1285 cm^{-1}. [^{1}H]NMR: δ 0.90 (t, 3H, J = 6.5 Hz, $CH_2C\underline{H}_3$), 1.10 (s, 3H, CH_3C isomer Z), 1.18 (s, 3H, CH_3C isomer E), 1.16 (d, 3H, J = 7.5 Hz, $C\underline{H}_3CH$ isomer Z), 1.21 (d, 3H, J = 7.5 Hz, $C\underline{H}_3CH$ isomer E), 1.1–2.0 (c, 13H, $6CH_2$ and CH). MS m/z (relative inten-

sity): 197 (M^+, 5), 180 (10), 154 (20), 142 (17), 141 (100), 126 (17), 124 (17), 113 (10), 109 (11).

Beckmann Fragmentation to Olefinic Nitriles ***6***. The procedure described by Marshall et al. (1970) was used. Thus, a mixture of 1.5 g (7.6 mmol) of oxime ***5*** and 3.3 g (17 mmol) of *p*-toluensulfonyl chloride in 5 ml of anh. pyridine was heated to reflux for 3 hr, cooled to room temperature, and quenched by pouring over 50 ml of ice water. After extraction with hexane (3× 50 ml), the combined organic layers were washed with brine and dried ($MgSO_4$). The solvent was removed under vacuum to furnish a brown oil, which was distilled to yield 0.87 g (64%) of the isomeric olefinic nitriles **6**, bp 90–95°C/0.1 torr. In addition to the major isomers obtained, which contained the expected trisubstituted double bonds on both sides of the methyl group at C-6, the isopropylidene derivative (δ 4.71) was also detected as minor compound.

IR: ν 2920, 2230, 1450, 1380 cm^{-1}. [^{1}H]NMR: δ 0.85 (t, 3H, J = 7 Hz, $CH_2C\underline{H}_3$), 1.25 (d, 3H, J = 7.7 Hz, $C\underline{H}_3CH$), 1.2–1.8 (c, 9H, $3CH_2CC$ and $CH_3C{=}C$), 1.8–2.3 (m, 4H, $2CH_2C{=}C$), 2.4 (m, 1H, CHCN), 5.05 (t, 1H, J = 6.0 Hz, CH=C). MS (major isomer) *m/z* (relative intensity): 179 (M^+, 7), 164 (21), 151 (57), 150 (35), 136 (46), 122 (28), 109 (20), 108 (100), 97 (12), 95 (11), 94 (18), 69 (15), 67 (11), 55 (18), 41 (14).

Reduction of Nitriles ***6*** *to Aldehydes* ***7***. To a magnetically stirred solution of 0.54 g (3 mmol) of mixture of nitriles **6** in 10 ml of anh. hexane was added, dropwise at −78°C, 3.35 ml of a 20% DIBAH solution in hexane (3.3 mmol). The solution was stirred at this temperature for an additional 30 min., warmed to room temperature, and further stirred for 2 hr. The mixture was poured carefully over 35 ml of a 3 M H_2SO_4 solution with stirring. The organic layer was decanted, and the aqueous phase was extracted with hexane (3× 40 ml). The organic extracts were combined and washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was distilled in a bulb-to-bulb distillation apparatus to give 0.45 g (83%) of mixture of aldehydes **7**, bp 100–104°C/0.1 torr.

IR: ν 2920, 1725 cm^{-1}. [^{1}H]NMR δ 0.85 (t, 3H, J = 5.5 Hz, $CH_2C\underline{H}_3$), 1.1 (d, 3H, J = 7.2 Hz, $C\underline{H}_3CH$), 1.2–1.8 (c, 9H, $3CH_2CC$ and $CH_3C{=}C$), 1.8–2.1 (m, 4H, $2CH_2C{=}C$), 2.3 (m, 1H, $C\underline{H}CHO$), 5.08 (t, 1H, J = 6.0 Hz, CH=C), 9.60 (d, 1H, J = 2.4 Hz, CHO). MS (major isomer) *m/z* (relative intensity): 182 (M^+, 8), 164 (28), 135 (15), 126 (50), 125 (24), 124 (100), 109 (59), 97 (20), 95 (100), 83 (20), 82 (28), 81 (37), 69 (38), 67 (28), 55 (53), 41 (33).

5,9-Dimethylheptadecane ***(1)***. In a flame-dried, three-neck, 50-ml, round-bottom flask equipped with magnetic stirrer, nitrogen inlet, and gas bubbler was placed 1.6 g (3.6 mmol) of *n*-heptyltriphenylphosphonium bromide in 15 ml of anh. THF. The mixture was cooled to −78°C and 3.3 ml of 1 M *n*-BuLi in

hexane (3.3 mmol) was added. After stirring at this temperature for 30 min, the hydrogen evolution had ceased. Then 0.45 g (2.47 mmol) of a mixture of aldehydes **7** in 2 ml of anh. THF was added and the reaction mixture stirred for an additional 30 min at −78°C and 1 hr at room temperature. After quenching with 25 ml of a 1 M H_2SO_4 soln., the organic layer was separated and the aqueous phase extracted with hexane (3× 20 ml). The organic phases were combined, washed with brine, and dried ($MgSO_4$) to leave a residue, after evaporation of the solvent, that was purified by column chromatography on silica gel eluting with hexane. The resulting oil was distilled in a bulb-to-bulb distillation apparatus to afford 0.40 g (60%) of mixture of the corresponding diunsaturated olefins, bp 119–123°C/0.1 torr.

IR: ν 3020, 2995, 2920, 1450, 1375 cm^{-1}. [^{1}H]NMR δ 0.90 (t, 6H, J = 6.5 Hz, $2CH_2C\underline{H}_3$), 0.95 (d, 3H, J = 6.5 Hz, $C\underline{H}_3CH$), 1.1–1.5 (b, 14H, $7CH_2CC$), 1.5–1.75 (dm, 3H, $CH_3C{=}C$), 1.8–2.2 (m, 6H, $3CH_2C{=}C$), 2.45 (m, 1H, CHC=C), 4.95–5.5 (m, 3H, 3CH=C). MS (major isomer) m/z (relative intensity): 264 (M^+, 15), 207 (29), 180 (22), 179 (49), 166 (20), 165 (32), 151 (25), 124 (44), 123 (37), 111 (23), 110 (38), 109 (71), 97 (22), 96 (37), 95 (100), 83 (29), 89 (23), 81 (67), 69 (52), 68 (23), 67 (22), 55 (41), 41 (20).

A mixture of 0.3 g (1.13 mmol) of the olefins, 30 mg of 10% Pd/C, 3 ml of THF, and 8 ml of methanol was hydrogenated at atmospheric pressure and room temperature. When the required amount of hydrogen had been absorbed, the catalyst was removed by filtration and the solvent evaporated off under vacuum. The resulting residue was purified by column chromatography on silica gel eluting with hexane and distilled in a bulb-to-bulb distillation apparatus to yield 0.26 g (86%) of hydrocarbon **1** (>98% on GLC analysis).

IR: ν 2920, 1460, 1375 cm^{-1}. [^{1}H]HMR δ 0.83 (d, 6H, J = 6.4 Hz, 2 $C\underline{H}_3CH$), 0.90 (t, 6H, J = 6.4 Hz, $2C\underline{H}_3CH_2$), 1.0–1.7 (b, 28H, $13CH_2$, and 2CH). MS m/z (relative intensity): 268 (M^+, 12), 253 (12), 239 (7), 211 (50), 210 (12), 183 (16), 155 (56), 154 (25), 141 (20), 140 (43), 127 (12), 113 (12), 112 (11), 99 (16), 97 (11), 85 (64), 84 (24), 71 (48), 70 (13), 69 (15), 57 (87), 56 (21), 55 (30), 43 (100), 41 (56).

5,9-Dimethyloctadecane (2). Following the same procedure described for the synthesis of **1**, starting from 1.30 g (2.86 mmol) of *n*-octyltriphenylphosphonium bromide, 2.6 ml of 1 M *n*-BuLi (2.6 mmol) in hexane, and 0.4 g (2.2 mmol) of aldehydes **7**, the corresponding mixture of intermediate olefins (0.41g, 67%) was obtained after purification on silica gel.

IR: ν 3020, 2995, 2920, 1450, 1375 cm^{-1}. [^{1}H]NMR δ 0.90 (t, 6H, J = 6.5 Hz, $2C\underline{H}_3CH_2$), 0.95 (d, 3H, J = 6.5 Hz, $C\underline{H}_3CH$), 1.1–1.5 (b, 16H, $8CH_2CC$), 1.5–1.8 (dm, 3H, $CH_3C{=}C$), 1.8–2.2 (m, 6H, $3CH_2C{=}C$), 2.45 (m, 1H, CHC=C), 5.0–5.5 (m, 3H, 3CH=C). MS (major isomer) m/z (relative intensity): 278 (M^+, 15), 221 (18), 194 (22), 193 (38), 165 (36), 151 (29),

124 (59), 123 (39), 111 (25), 110 (59), 109 (72), 97 (21), 96 (26), 95 (100), 83 (23), 82 (29), 81 (74), 69 (55), 68 (24), 67 (24), 55 (48), 41 (25).

Hydrogenation of 0.15 g (0.5 mmol) of a mixture of olefins, in the presence of 15 mg of 10% Pd/C in 5 ml of THF and 10 ml of methanol, afforded, under the above reaction conditions, 0.13 g (86%) of compound **2** after purification on silica gel (>98% purity on GLC analysis), bp 125–126°C/0.1 torr.

IR: ν 2920, 1460, 1375 cm^{-1}. [^{1}H]NMR δ 0.81 (d, 6H, J = 6.4 Hz, 2C$\underline{H_3}$CH), 0.90 (t, 6H, J = 6.4 Hz, 2C$\underline{H_3}CH_2$), 1.0–1.7 (b, 30H, 14CH_2, and 2CH). MS m/z (relative intensity): 282 (M^+, 9), 267 (11), 253 (5), 225 (44), 224 (13), 197 (12), 196 (8), 155 (58), 154 (57), 127 (9), 126 (12), 113 (12), 112 (9), 99 (15), 85 (57), 84 (24), 71 (44), 70 (11), 69 (13), 57 (88), 56 (21), 55 (31), 43 (100), 41 (43).

Field Tests. The field trials were carried out in infested apple orchards near the villages of Roselló (Lérida) and Mas Badía (Gerona) (June–September 1988–1989). Delta traps containing the lures were hung on trees at a height of 1.8 m and 25–30 m apart. Polyethylene vials (3 cm high × 1.1 cm ID) containing mixtures of 1 mg of compound **1** and minor amounts of **2** were used as dispensers. The traps were arranged in randomized blocks and rotated twice a week. Three replicates of each formulation were tested at each site. Trap catches were subjected to $\sqrt{x+1}$ transformation followed by analysis of variance, and the data were analyzed statistically for significance according to LSD and Tuckey's HSD test.

RESULTS AND DISCUSSION

In preliminary experiments carried out in 1986–1987, 450 1- to 2-day-old virgin females were macerated in nanograde methylene chloride for 1 hr. After filtration, the extract was carefully concentrated under a gentle stream of nitrogen and subjected to a flash distillation under high vacuum (0.01 torr) to remove any contaminating lipidic material. The volatile fraction, which turned out to be as active as the crude extract, was fractionated on silica gel eluting with mixtures of hexane–ether according to the procedure of Buser and Arn (1975). Among the fractions tested, only those eluted with hexane and hexane–ether 5% were significantly active in field trials. On the other hand, 150 female-equivalents were subjected to a series of microchemical reactions such as hydrogenation (H_2, Pd/C), saponification (KOH/MeOH), acetylation (Ac_2O/py), and reduction (LAH/ether) with no appreciable loss of activity. The [^{1}H]NMR spectrum of ca. 20 μg of the most active fraction in C_6D_6 showed, as noticeable absorptions, a doublet at δ 0.88 (J = 7.2 Hz), a distorted triplet at δ 0.93 (J = 7.0 Hz), and a broad complex absorption centered at δ 1.29. These results point out the presence of saturated hydrocarbon(s) in the active extract as described previously (Francke et al., 1987).

In order to look for possible minor components that might enhance the male attractant activity of the major compound **1**, a careful analysis of the active material was undertaken. Gas chromatographic analysis of the volatiles released by 250 virgin calling females, on three different fused silica capillary columns (A, B, and C, see above), showed the presence of two compounds in 92:8 to 96:4 ratio. The retention times of both compounds were the following: 30.75 and 33.85 min in column A, 25.48 and 29.03 min in column B, and 26.40 and 30.28 min in column C. It must be noted that neither compound **1** nor **2** was found in the volatile extract of 102 unmated males under the chromatographic conditions specified above (Figure 1).

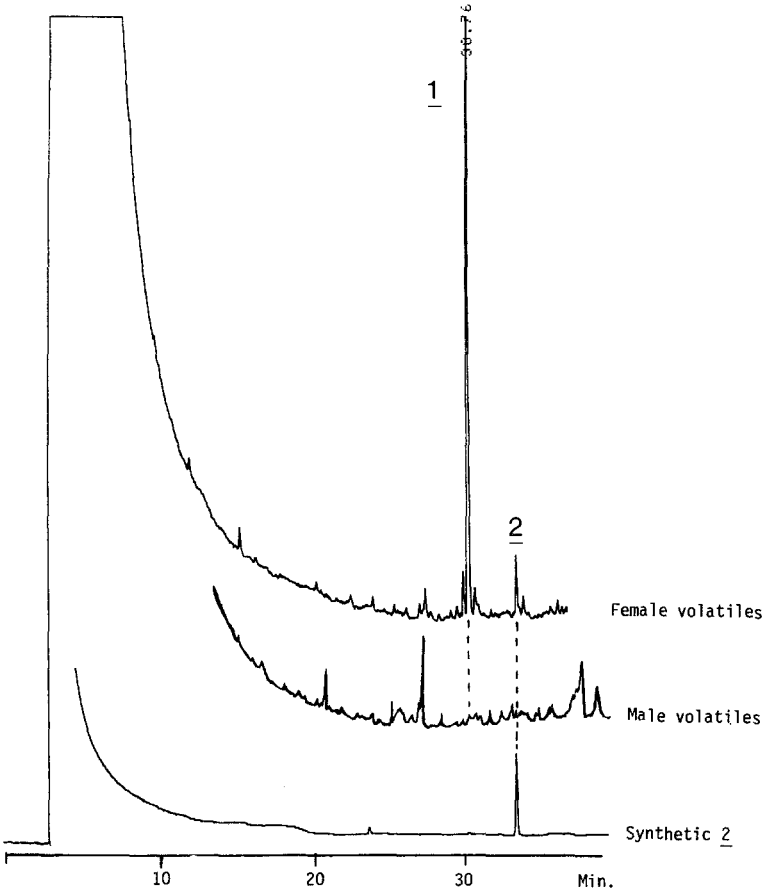


FIG. 1. (Upper) GC trace of the female volatile extract of *Leucoptera malifoliella* using column A (see text). (Middle) GC trace of the male volatile extract of *Leucoptera malifoliella* under the same chromatographic conditions. (Lower) GC trace of the synthetic minor component **2**.

The EI mass spectrum of the major compound showed the highest mass ion at *m/z* 268 and diagnostic peaks at *m/z* 253, 211, and 155, suggesting a 5,9-dimethyl branched saturated hydrocarbon (Pomonis et al., 1980). On the other hand, the CI/CH_4 mass spectrum showed the base peak at *m/z* 267, corresponding to M^+-1, in agreement with the previously assigned molecular weight. Finally, comparison of the chromatographic retention time on columns A, B, and C with a synthetic sample confirmed the structure of the major component as 5,9-dimethylheptadecane (**1**), as already described (Francke et al., 1987). Compound **1** has been utilized by us to monitor the population density of the pest for the field trials, as well as to establish three to four annual overlapping generations in Lérida province.

On the other hand, the EI mass spectrum of the minor compound showed the highest mass peak at *m/z* 282 along with other prominent, characteristic peaks at *m/z* 267, 225, and 155. The molecular weight of 282, corresponding to a $C_{20}H_{42}$ structure, was confirmed by the CI/CH_4 mass spectrum, which showed the base peak at *m/z* 281 (M^+-1). In addition, the peak at *m/z* 267, which suggested the favored loss of a methyl group from the molecular ion, supported a methyl-branched hydrocarbon structure. On the other hand, the ion of *m/z* 225 pointed to a $C_{16}H_{33}$ fragment, which implied a branch point at C-5, whereas that of *m/z* 155 was assigned to a $C_{11}H_{23}$ fragment resulting from the α cleavage on both sides of a ramification at C-9. This caused an enhancement of the peak in comparison with the same ion in the mass spectrum of **1**, wherein only one favored fragmentation with that mass is possible. Therefore, after considering the fragmentation patterns of other dimethyl-branched hydrocarbons (Pomonis et al., 1980), we finally assigned the structure of the minor compound as 5,9-dimethyloctadecane (**2**). In addition, a plausible biogenetic consideration is that the possible precursor of both compounds **1** and **2** might be a C-18 acid structure, whose carbonyl group would be lost to produce **1** or transformed into a methyl group by a reduction–elimination process to give rise to **2** (Francke, personal communication).

The assignment of the minor component **2** was confirmed by comparison of the chromatographic behavior (retention time) on columns A, B, and C (see above) and the EI and CI mass spectra with those of an authentic sample of **2** prepared by synthesis (Figures 1 and 2). The synthetic route to compounds **1** and **2** followed a modification of the procedure described by Kocienski and Ansell (1977) (Scheme 1). Thus, base-catalyzed alkylation of 2,6-dimethylcyclohexanone (**3**) with *n*-butyl bromide afforded ketone **4**, which, after transformation into the oxime **5**, was subjected to a Beckmann fragmentation according to the procedure described by Marshall et al. (1970). Treatment of the oxime **5** with *p*-toluensulfonyl chloride in pyridine at reflux furnished a mixture of nitriles **6** in good yield, with no trace of the corresponding lactam being detected. As shown by the [^{1}H]NMR spectrum, the mixture contained mainly the isomeric nitriles with the expected trisubstituted double bonds on both sides of the methyl

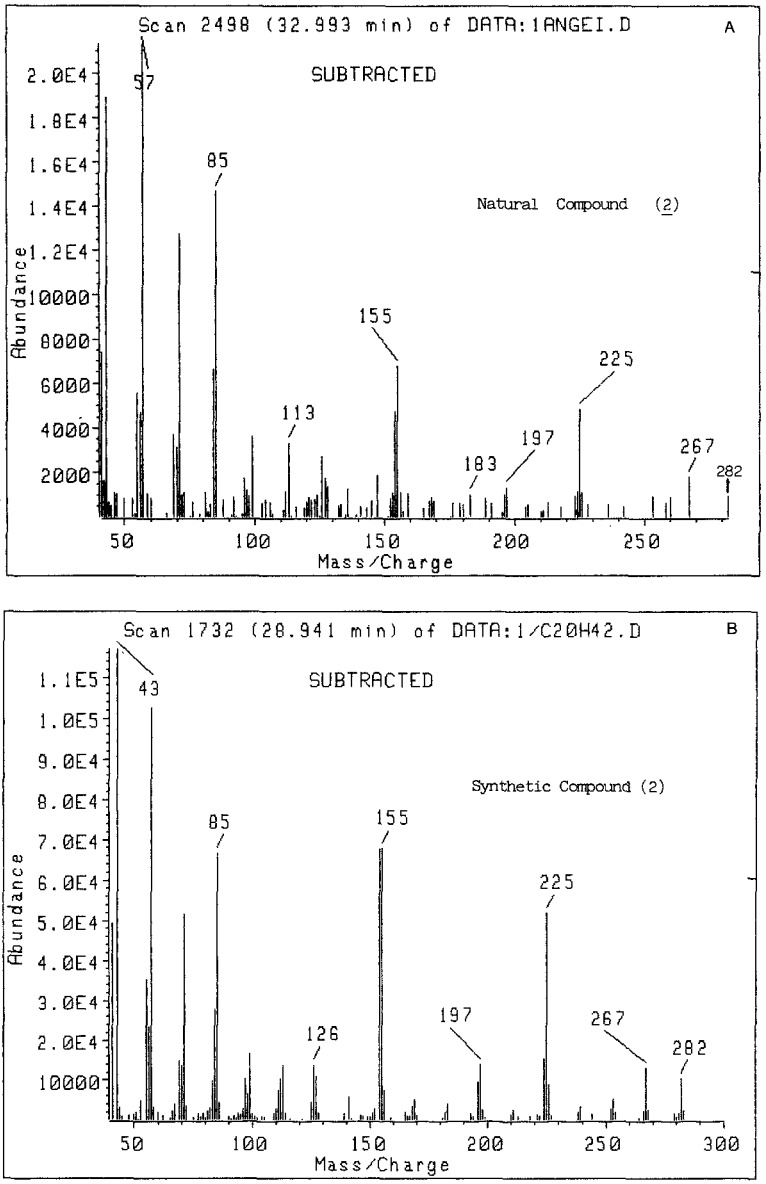


FIG. 2. (A) EI-MS of the natural minor component **2**. (B) EI-MS of the synthetic compound **2**.

group at C-5, although the presence of the corresponding isopropylidene isomer was also noted (δ 4.71) in minor amount (ca. 12%). Reduction of nitriles **6** with DIBAH in hexane at −78°C furnished a mixture of aldehydes **7**, which were transformed into compounds **1** and **2** by Wittig reaction with the required ylides followed by complete hydrogenation with Pd/C. The overall yield of both routes was ca. 12% from ketone **3**.

In preliminary field tests carried out in 1988, the minor compound **2** appeared to enhance the activity of the major component **1**. Thus, when compound **2** was mixed with **1** at 0.1–1% level, a significant increase of catches was observed in comparison with captures of compound **1** alone (Table 1). The synergistic effect was confirmed in new field experiments, run in 1989, wherein baits loaded with mixtures of compounds **1** and **2** in 100:1 to 100:5 ratios showed higher attractant activity than compound **1** alone (Table 2). However,

TABLE 1. CAPTURE OF *Leucoptera malifoliella* MALES WITH BLENDS OF COMPOUNDS **1** AND **2** (ROSELLÓ, LÉRIDA, JUNE–SEPTEMBER 1988)

Composition of lure (mg)			
1	**2**	Ratio **2:1**	Mean catch/trap/week[a]
1		0:100	60.6 b
1	0.001	0.1:100	117.2 a
1	0.01	1:100	109.2 a
	1	100:0	1.8 c

[a] Three replicates. Means followed by the same letter are not significantly different at $P = 0.05$ according to Tukey's HSD test.

TABLE 2. CAPTURE OF *Leucoptera malifoliella* MALES WITH MIXTURES OF COMPOUNDS **1** AND **2** (ROSELLÓ, LÉRIDA, JUNE–JULY 1989)

Composition of lure (mg)			
1	**2**	Ratio **2:1**	Mean catch/trap/week[a]
1		0:100	67.7 c
1	0.001	0.1:100	77.3 bc
1	0.01	1:100	84.0 ab
1	0.05	5:100	105.0 a
	1	100:0	3.5 d

[a] Three replicates. Means followed by the same letter are not significantly different at $P = 0.05$ according to LSD test.

TABLE 3. CAPTURE OF *Leucoptera malifoliella* MALES WITH BLENDS OF COMPOUNDS **1** AND **2** (MAS BADÍA, GERONA, JUNE–JULY 1989)

Composition of lure (mg)			
1	**2**	Ratio **2:1**	Mean catch/trap/week[a]
1		0:100	34.1 b
1	0.001	0.1:100	35.2 ab
1	0.01	1:100	36.8 ab
1	0.05	5:100	45.2 a
	1	100:0	3.4 c

[a]Three replicates. Means followed by the same letter are not significantly different at $P = 0.05$ according to LSD test.

in orchards with a lower level of infestation (Mas Badía, 1989), the synergism was noted only in lures containing 5% of the minor component **2** (Table 3), clearly the best formulation found in the former field test. In all cases, the intrinsic attractant activity of **2** was very low.

In summary, a new minor component **2** has been found in the female volatile extract of *Leucoptera malifoliella*. The compound has been identified as 5,9-dimethyloctadecane based on its spectroscopic properties and chromatographic behavior in comparison with an authentic synthetic sample. The structure of the major component as 5,9-dimethylheptadecane also has been confirmed after comparison with an independently prepared **1**. The synthesis of both compounds has been carried out through a short route from 2,6-dimethylcyclohexanone. In field tests, the minor component **2** appears to act as a synergist of the major compound **1** when mixed with the latter in a 100:0.1–5 ratio.

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