87. Synthesis of Three Jasmin Constituents *via* a Central Intermediate[1])

by **Paul Dubs** and **Rita Stüssi**

Givaudan Ltd, Research Company, 8600 Dübendorf-Zürich

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Summary

Syntheses of jasmone (**1**), methyl jasmonate (**3**) and γ-jasmolactone (**2**) are reported, (*Z*)-nona-1,6-dien-3-one (**4**) serving as common intermediate.

Past analytical efforts have revealed that a considerable number of olfactively interesting constituents of the essential oil of jasmin flowers (*Jasminum grandiflorum* L.) contain (*Z*)-double-bonds in unbranched, aliphatic side chains as a salient structural feature[2]). Practically all these components are either ketones or lactones. Most prominent among them are jasmone (**1**), γ-jasmolactone (**2**) and methyl jasmonate (**3**).

Considerable effort has been devoted to the synthesis of jasmone (**1**)[3]) and methyl jasmonate (**3**) [6], whereas γ-jasmolactone (**2**) is synthetically much less [2] explored. The cyclopentanoid structures **1** and **3** exhibit (*Z*)-pent-2-enyl substructures, but differ in their degree of ring unsaturation. Lactone **2** incorporates a (*Z*)-hex-3-enyl side chain instead. It seems very likely that this relationship has its biogenetic reasons, but no efforts to elucidate the biogenesis of compounds **1**–**3** have been reported so far. However, the co-occurrence of polyunsaturated straight chain all (*Z*)-fatty acid derivatives like methyl linolenate [7] in jasmin oil suggests formation of **1**–**3** from such precursors [1][4]) in the flower.

Such reasonings led us to conceive short syntheses for compounds **1**–**3** which incorporate in different ways the C_9-unit **4**. By *Michael*-additions of formal acyl anions of the types depicted in *Scheme 2* we should arrive at intermediates suitable for further elaboration to compounds **1**–**3**. For convenience and simplicity our intent to effect transformations a) and b) was to use, among the possible versatile [9]

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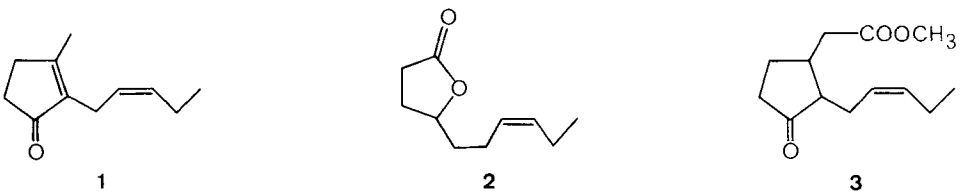
[1]) These results were reported by *P. Dubs* at the Autumn session of the Swiss chemical Society (Oct. 20, 1973) in Lugano.

[2]) Review and discussion: [1]. Since then, further compounds exhibiting the structural characteristics mentioned have been detected in this essential oil [2] [3]. An article on the composition of jasmin oil has recently been published [4].

[3]) *Van der Gen* [1] and *Ellison* [5] give good, although not entirely complete, accounts of jasmone syntheses.

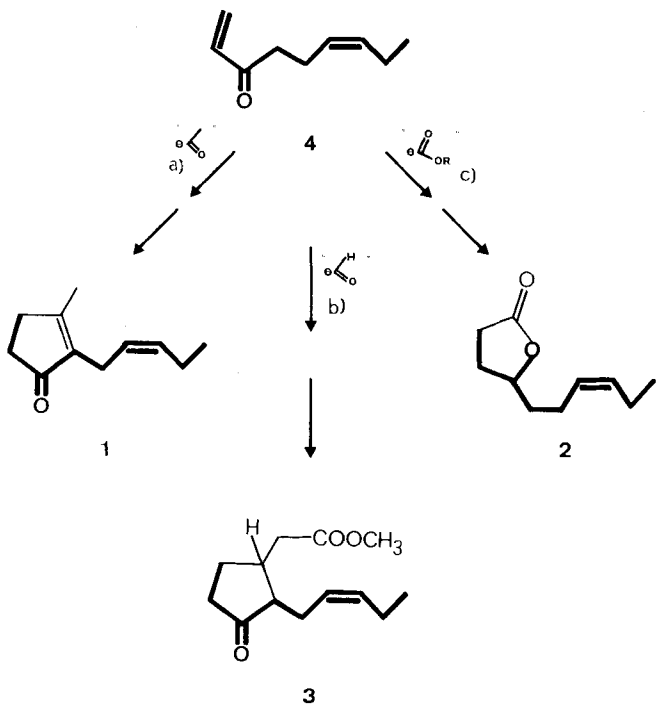
[4]) Similar cyclisations of unsaturated fatty acids to cyclopentanoid structures are well established in the closely related field of prostaglandins [8].

Scheme 1



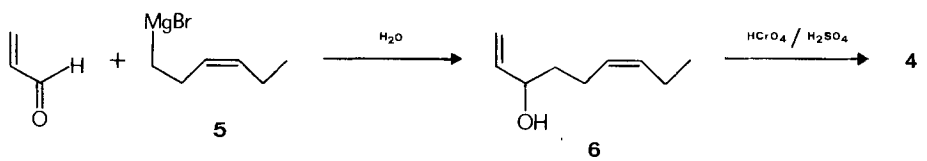
1 2 3

Scheme 2



1 2 3

Scheme 3



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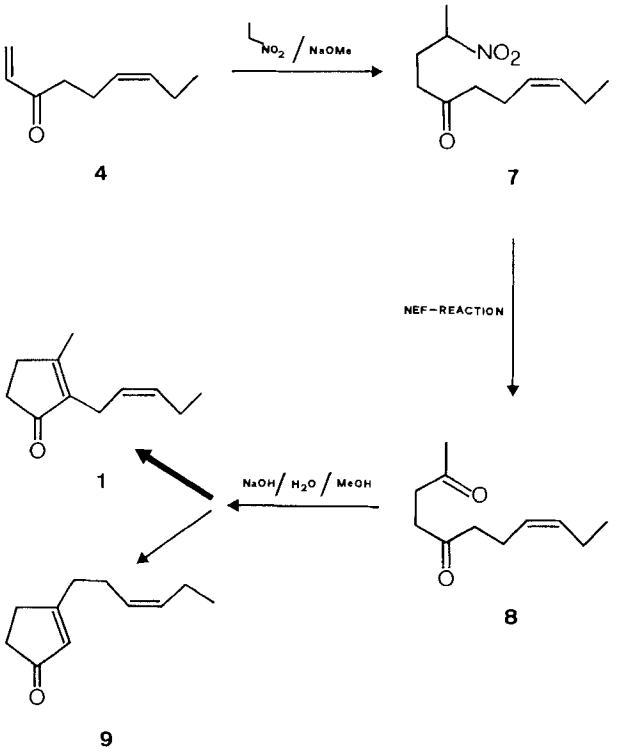
masked acyl anions, nitro compounds in their deprotonated state [10]. Cyanide ion is the simplest reagent for process c).

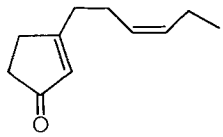
This work had to begin with the synthesis of (Z)-nona-1,6-dien-3-one (**4**). Following *Takei et al.* [11] addition of **5** to acrolein gave alcohol **6**, which was subjected to a two-phase *Jones* oxidation, at $-15°$ *(Scheme 3).* If the temperature was raised

Scheme 4. *Synthesis of* (Z)-*jasmone* (**1**)



to +30°, isomerization to the (*E*)-isomer of **4** took place to an extent of 30%. (*Z*)-Nona-1,6-dien-3-one (**4**) was condensed with deprotonated nitroethane, to yield the nitro-ketone **7**[5]) which was transformed to the diketone **8** by the *Nef* reaction [10]. The reaction temperature was kept at − 15° to avoid isomerization of the side chain double-bond of **8**. Diketone **8** was subsequently cyclized to jasmone (**1**) *via* an intramolecular aldolization, following *Hunsdiecker* [13] *(Scheme 4)*.

GC. investigation of the crude cyclization products showed that, in addition to the expected jasmone (**1**), *ca.* 3% - with respect to **1** - of a higher boiling compound **9** was formed, arising from the alternate possibility of aldolization-dehydration of 2,5-diketone **8**. This observation is at variance with earlier literature [14]. The ketone **9** was isolated by fractional distillation followed by GC. and its structure was confirmed by independent synthesis according to *McCurry* [15].



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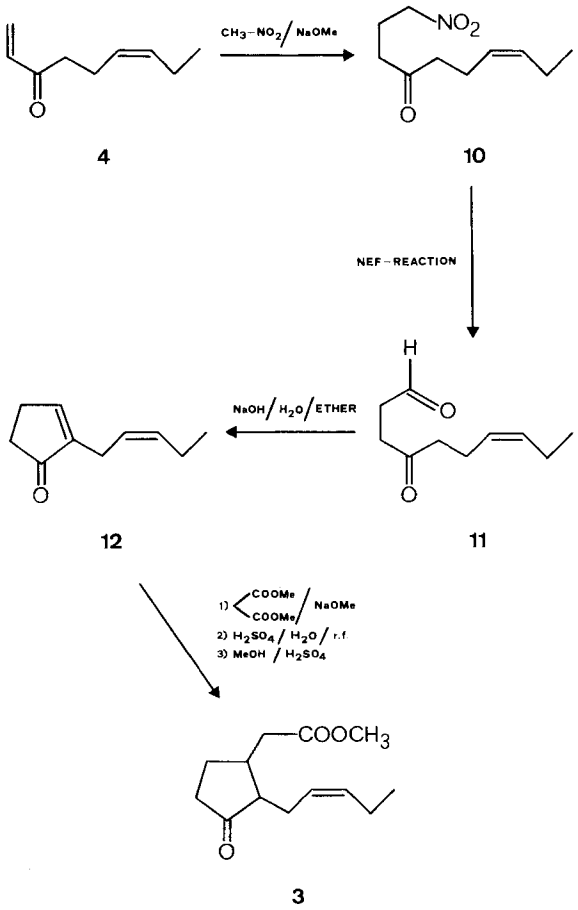
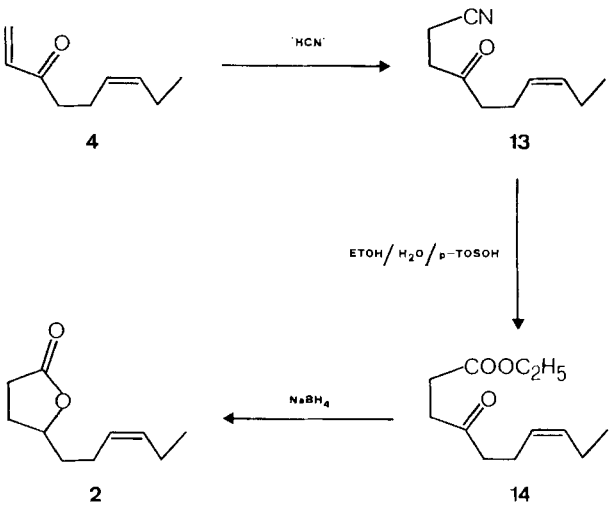
[5]) A related nitro intermediate has been converted to jasmone (**1**) by *McMurry et al.* [12].

In analogy to the synthesis of jasmone (**1**) *(Scheme 4)*, addition of nitromethane to the dienone **4** led to the primary nitro derivative **10** which was subsequently treated under *Nef* conditions to give the expected keto-aldehyde **11**. If ethanol was used as co-solvent in the acid hydrolysis of the sodium salt of **10**, the diethylacetal of **11** was formed in high yield, in spite of the small quantity of alcohol in relatively high amounts of water. These observations are in good agreement with *Jacobson* [16], who prepared acetals from primary nitro compounds under very similar conditions. The *Nef* reaction **10** → **11** was instead run in tetrahydrofuran as co-solvent. Base-induced intramolecular aldolization-dehydration of ketoaldehyde **11** gave the cyclopentenone derivative **12**. Optimal results were obtained when sodium hydroxide was used in ether/water. The remaining reactions, leading from **12** to **3**, are standard procedures [6 d)]: *Michael*-addition of methyl malonate, hydrolysis of the diester to the corresponding diacid, decarboxylation and esterification to yield methyl jasmonate (**3**) *(Scheme 5)*.

Scheme 5. *Synthesis of* (Z)-*methyl jasmonate* (**3**)



Scheme 6. *Synthesis of* (Z)-*γ-jasmolactone* (**2**)



The nonadienone **4** was conveniently transformed to the ketonitrile **13** by using the cyanohydrin of acetone as a hydrogen cyanide source [17]. Compound **13** was converted to the corresponding ethyl ester with *p*-toluenesulfonic acid in ethanol. Subsequent reduction of this ester with sodium borohydride led directly to *γ*-jasmolactone (**2**) without isolation of the *γ*-hydroxy ester intermediate.

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Experimental Part

General. – ^{1}H-NMR. spectra were recorded on a *Varian* XL-100A instrument (100 MHz), in $CDCl_3$ with TMS (0 ppm) as internal standard; abbreviations: *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quadruplet, *qi* = quintuplet, *m* = multiplet, br. = broad, *J* = spin-spin coupling constant (Hz). IR. spectra were measured on a *Perkin-Elmer* 257 spectrometer; characteristic maxima are given in cm^{-1}. Mass spectra were recorded on a *Varian* CH-5 spectrometer, using an inlet temperature of 150° and an ionisation energy of 70 eV; the intensity of the molecular ion and of the 8 most intense fragment ions are given in % of the base peak. Gas liquid chromatography (GC.) was performed on a *Carlo Erba* Fractovap GI instrument, using Carbowax 20 M, 2% on Chromosorb G H.P., 80–100 mesh (3 mm × 3 m).

1. Synthesis of (*Z*)-nona-1,6-dien-3-one (4). – (Z)-*Nona-1,6-dien-3-ol* (**6**). A *Grignard* reagent, prepared from Mg (6 g, 0.25 mol) and (*Z*)-1-bromohex-3-ene [14b] (40.75 g, 0.25 mol) in 75 ml abs. ether, was cooled to −15°, and freshly distilled acrolein – stabilized with 0.2% hydroquinone – (15.4 g, 0.275 mol) in 35 ml abs. ether were added dropwise with stirring. Stirring was continued at −15° for 30 min after addition. The reaction mixture was slowly poured into 250 ml of a well stirred 50% aq. NH_4Cl-solution, kept at 0°. After addition of 230 ml of 1N H_2SO_4 at 0°, the solution (pH *ca.* 2–3) was extracted with ether (4× 150 ml) at 0°. The combined extracts were washed twice with a saturated $NaHCO_3$-solution and dried (Na_2SO_4). After evaporation of the solvent at 40°/11 Torr, 29.02 g (83%) of crude **6** were obtained as a colourless oil, pure by GC. and TLC. – IR. (liq.): 3400, 1650, 1460, 1425, 1050,

995, 945, 830. – ^{1}H-NMR.: 6.25–4.95 (*m*, 5 H, H_2C=CH and HC=CH); 4.13 (*qa*, J=6, 1H, CH–O); 2.44–1.83 (br., 5 H, CH_2–C=C–CH_2 and OH); 1.80–1.33 (*m*, 2 H, CH_2); 0.97 (*t*, J=7.5, 3 H, CH_3). – MS.: 122 (*M*, 12), 57 (100), 41 (95), 55 (80), 70 (62), 79 (61), 68 (58), 93 (46), 83 (32).

(Z)-*Nona-1,6-dien-3-one* (**4**). Crude (*Z*)-nona-1,6-dien-3-ol (**6**) (28.8 g, 0.206 mol) in 290 ml ether was cooled at –20°, while 51.4 ml of a 2.672N *Jones* reagent[6]) were slowly added at ≤ –15° with good stirring. After addition, stirring was continued at –15°–20° for a further 35 min. The reaction mixture was slowly poured into ice/water and extracted at 0° with ether (3×200 ml). The organic extracts were washed once with 100 ml of a saturated $NaHCO_3$-solution, and dried (Na_2SO_4). Hydroquinone (150 mg) was added and half the solvent was removed at normal pressure. This solution was reoxidized[7]) with 17.2 ml of the *Jones* reagent under the above conditions. 2-Propanol (4 ml) was added at –15° to destroy excess reagent, and the reaction mixture worked up as before. After addition of hydroquinone (150 mg), the solvent was removed at normal pressure, to yield 22.0 g (77.5%) of crude[8]) **4** as a colourless oil, pure by GC. and TLC. – IR. (liq.): 1710, 1690, 1625, 1410, 1100, 1040, 990, 970. – ^{1}H-NMR.: 6.42–5.62 (*m*, 3 H, H_2C=CH); 5.56–5.17 (*m*, 2 H, HC=CH); 2.83–1.74 (*m*, 6 H, 3 CH_2); 0.95 (*t*, J=7.5, 3 H, CH_3). – MS.: 138 (*M*, 1), 55 (100), 41 (65), 39 (41), 68 (30), 81 (18), 109 (17), 95 (14), 123 (4).

2. Synthesis of (*Z*)-Jasmone (**1**). – (Z)-*2-Nitroundec-8-en-5-one* (**7**). To crude (*Z*)-nona-1,6-dien-3-one (**4**) (21.8 g, 0.158 mol) in 220 ml methanol and 59.3 g nitroethane (passed through basic aluminum oxide before use), 0.5 g of solid sodium methanolate were added. After heating at reflux under argon for 10 min, the solvent was almost completely evaporated. Saturated $NaHCO_3$-solution (150 ml) was added and the whole extracted with ether (3×100 ml). The organic extracts were washed once with brine, dried (Na_2SO_4) and concentrated at 50°/11 Torr to obtain 34.18 g (100%) of crude oily **7**, pure by GC. and TLC. – IR. (liq.): 1720, 1550, 1360, 1080, 975, 870. – ^{1}H-NMR.: 5.58–5.18 (*m*, 2 H, HC=CH); 4.60 (*sextet*, J=7, 1H, H–C–NO_2); 2.70–1.90 (*m*, 10 H, 5 HC_2); 1.52 (*d*, J=7, 3 H, CH_3); 0.98 (*t*, J=7, 3 H, CH_3). – MS.: 213 (*M*, 0), 55 (100), 41 (67), 83 (63), 68 (50), 165 (30), 167 (26), 111 (23), 101 (20).

(Z)-*Undec-8-en-2,5-dione* (**8**). A solution of crude (*Z*)-2-nitroundec-8-en-5-one (**7**) (34 g, 0.16 mol) in 510 ml ethanol and 510 ml 2N NaOH was added dropwise with good stirring to 1190 ml of 10N H_2SO_4 at –10°. The reaction mixture was extracted with hexane (4×150 ml) at –10°. The organic layers were washed once with saturated $NaHCO_3$-solution, and dried (Na_2SO_4). The solvent was removed by evaporation at 40°/11 Torr, to obtain 20.74 g (72%) of crude **8** as an oil, pure by GC. – IR. (liq.): 1715, 1660, 1410, 1385, 1180, 1100, 1030, 1000, 975, 930. – ^{1}H-NMR.: 5.65–5.05 (*m*, 2 H, HC=CH); 2.69 (*s*, 4 H, CO–CH_2–CH_2–CO); 2.20 (*s*, 3 H, CH_3–CO); 2.70–1.70 (*m*, 6 H, 3 CH_2); 0.94 (*t*, J=7.5, 3 H, CH_3). – MS.: 182 (*M*, 2), 43 (100), 71 (55), 99 (55), 55 (40), 95 (39), 124 (18), 114 (17), 83 (15).

(Z)-*Jasmone* (**1**). Crude (*Z*)-undec-8-ene-2,5-dione (**8**) (20.5 g, 0.12 mol) was refluxed for 5 h under argon in a mixture of 50 ml ethanol and 180 ml 0.5N NaOH. The solution was cooled to RT. and extracted with pentane (3×100 ml). The organic phases were washed once with brine, and dried (Na_2SO_4). The solvent was evaporated at 50°/11 Torr. 18.5 g of an oily brownish crude product was obtained and distilled through a *Vigreux* column, to give 12.9 g (65%) of pure (*Z*)-jasmone (**1**), n_D^{20} = 1.4989. The last fractions (2 g; b.p. 67–68°/0.025 Torr) of this distillation contained the isomer **9** in enriched form. Pure **9** was obtained by prep. GC. (Carbowax 20M on Chromosorb G)[9]).

(Z)-*Jasmone* (**1**): UV. (EtOH): 234 nm (12640). – IR. (liq.): 1700, 1650, 1420, 1385, 1340, 1305, 1190, 1075, 1035, 975, 840. – ^{1}H-NMR.: 5.70–5.10 (*m*, 2 H, HC=CH); 3.00 (br. *d*, J=5.5, 2 H, CH_2); 2.58–1.90 (*m*, 6 H, 3 CH_2); 2.08 (*s*, 3 H, CH_3); 0.98 (*t*, J=7.5, 3 H, CH_3). – MS.: 164 (*M*, 61), 41 (100), 39 (97), 79 (83), 91 (57), 53 (53), 55 (48), 110 (47), 149 (38).

Isomer **9**: UV. (EtOH): 228 nm (15010). – IR. (liq.): 1710, 1675, 1615, 1440, 1410, 1230, 1185, 855, 840. – ^{1}H-NMR.: 6.00 (br., 1H, CH=); 5.70–5.10 (*m*, 2 H, HC=CH); 2.80–1.80 (*m*, 10 H, 5 CH_2); 1.00 (*t*, J=7.5, 3 H, CH_3). – MS.: 164 (*M*, 4), 96 (100), 41 (95), 69 (50), 53 (18), 79 (13), 107 (8), 122 (8), 136 (3).

3. Synthesis of (*Z*)-methyl jasmonate (**3**). – (Z)-*1-Nitrodec-7-en-4-one* (**10**). To crude (*Z*)-nona-1,6-dien-3-one (**4**) (38.5 g, 0.279 mol), dissolved in a mixture of 550 ml methanol and 126 g nitromethane

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[6]) Reagent: 262.2 g of CrO_3 and 230 ml of conc. sulfuric acid are diluted to 1 l with water.

[7]) 20–25% of the starting material **6** remained after the first oxidation (NMR., GC.).

[8]) No starting material **6** could be detected after this procedure.

[9]) The ratio of **9** to (*Z*)-jasmone (**1**) was estimated (GC.) 3:97 in the crude cyclization product.

(passed through basic aluminum oxide before use), 1.26 g of solid sodium methanolate were added. After warming to 30° for 15 min under argon, the solvent was almost completely evaporated *in vacuo*, to obtain 55.25 g (100%) of crude **10**. – IR. (liq.): 1720, 1555, 1440, 1420, 1370, 1110, 1075, 975. – ^{1}H-NMR.: 5.65–5.10 (*m*, 2 H, HC=CH); 4.45 (*t*, *J* = 6, 2 H, CH_2–NO_2); 2.75–1.75 (*m*, 10 H, 5 CH_2); 0.98 (*t*, *J* = 7, 3 H, CH_3). – MS.: 199 (*M*, 0), 41 (100), 68 (75), 55 (51), 69 (50), 83 (33), 116 (21), 111 (19), 87 (18).

(Z)-*4-Oxo-dec-7-en-1-al* (**11**). The solution of crude (*Z*)-1-nitrodec-7-en-4-one (**10**) (52 g, 0.362 mol) in a two-phase mixture of 730 ml tetrahydrofuran and 730 ml 2N NaOH was added dropwise, and with good stirring, to 1700 ml of 10N H_2SO_4 at −10°. The reaction mixture was extracted with hexane (4 × 300 ml) at −10°. The organic layers were once washed with saturated $NaHCO_3$-solution, combined, and dried (Na_2SO_4). The solvent was removed by evaporation at 40°/11 Torr. The crude residue (41.42 g) was chromatographed on 900 g silica gel (*Merck*, 0.063–0.20 mm) with hexane/ether 20:1, 9:1 and 4:1. 27.5 g (45.2%) of pure (GC. and TLC.) **11** were obtained. – IR. (liq.): 2730, 1710, 1410, 1390, 1370, 1100, 1070, 1030, 980, 870. – ^{1}H-NMR.: 8.55 (*s*, 1H, CHO); 5.67–5.00 (*m*, 2 H, HC=CH); 2.73 (*s*, 4 H, CO–CH_2–CH_2–CO); 2.70–1.72 (*m*, 6 H, 3 CH_2); 0.96 (*t*, *J* = 7.5, 3 H, CH_3). – MS.: 168 (*M*, 6), 85 (100), 41 (79), 55 (60), 68 (51), 95 (34), 124 (32), 100 (28), 111 (16).

(Z)-*2-(Pent-2-enyl)cyclopent-2-en-1-one* (**12**). (*Z*)-4-Oxo-dec-7-en-1-al (**11**) (13.5 g, 0.08 mol) dissolved in 70 ml ether was added to 70 ml of 2N *aq.* NaOH. The resulting two-phase mixture was vigorously stirred at RT. for 20 h, then extracted with pentane (3 × 50 ml). The organic phases were washed once with brine, and dried (Na_2SO_4). The solvent was evaporated at 40°/11 Torr, to obtain 12.08 g of an oily crude product which was distilled through a *Vigreux*-column, yielding 2.86 g (23.8%) of pure (GC., TLC.) **12**. – IR. (liq.): 1705, 1635, 1450, 1355, 1055, 1010, 800, 750. – ^{1}H-NMR.: 7.33 (*m*, 1H, CH=C–CO); 5.85–5.14 (*m*, 2 H, HC=CH); 2.90 (*m*, 2 H, =C–CH_2–C=); 2.75–2.28 (*m*, 4 H, cyclic CH_2–CH_2); 2.25–1.80 (*m*, 2 H, CH_2); 0.94 (*t*, *J* = 7.5, 3 H, CH_3). – MS.: 150 (*M*, 60), 39 (100), 79 (95), 55 (79), 41 (78), 121 (63), 91 (49), 96 (42), 65 (30).

(Z)-*Methyl jasmonate* (**3**). (*Z*)-2-(Pent-2-enyl)cyclopent-2-en-1-one (**12**) was converted to (*Z*)-methyl jasmonate (**3**) (overall yield: 71%), following *Büchi & Egger* [6d] for the transformation of 2-(pent-2-ynyl)cyclopent-2-en-1-one into methyl dehydrojasmonate *(Scheme 5)*. The spectral data of **3** (IR., NMR. and MS.) were in agreement with the literature [6d].

4. Synthesis of (*Z*)-γ-jasmolactone (**2**). – (Z)-*1-Cyano-non-6-en-3-one* (**13**). To crude (*Z*)-nona-1,6-dien-3-one (**4**) (2.76 g, 20 mmol) and acetone cyanohydrin (1.92 g, 22.6 mmol) in 7 ml methanol, 2 ml of 2N *aq.* Na_2CO_3 were added. After heating under reflux for 30 min, the reaction mixture was diluted with saturated *aq.* Na_2CO_3-solution, and extracted 3 times with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4), and the solvent was evaporated at 40°/11 Torr. The crude reaction product (2.9 g) was subjected to a bulb-to-bulb distillation (oven temp.: 110°) at 0.035 Torr, whereby 2.43 g (73.6%) of pure (GC.) **13** were obtained. – IR. (liq.): 2280, 1725, 1415, 1370, 1100. – ^{1}H-NMR.: 5.92–5.02 (*m*, 2 H, HC=CH); 3.03–1.80 (*m*, 10 H, 5 CH_2); 1.00 (*t*, *J* = 7.5, 3 H, CH_3). – MS.: 165 (*M*, 5), 68 (100), 41 (55), 55 (40), 82 (35), 98 (10), 95 (6), 111 (6), 136 (3).

(Z)-*4-Oxo-dec-7-enoic acid ethylester* (**14**). A solution of (*Z*)-1-cyano-non-6-en-3-one (**13**) (38.5 g, 0.233 mol) and *p*-toluenesulfonic acid monohydrate (49 g, 0.258 mol) in 50 ml ethanol was heated under reflux for 30 h. The reaction mixture was diluted with 2N *aq.* Na_2CO_3, and extracted 3 times with ether. The organic phases were washed twice with brine, and the solvent was evaporated at 40°/11 Torr. The crude product was distilled through a *Vigreux*-column, whereby 31.9 g (64.6%) of pure (GC.) **14** were obtained. – IR. (liq.): 1735, 1720, 1415, 1375, 1350, 1190, 1095, 1030, 850. – ^{1}H-NMR.: 5.67–5.00 (*m*, 2 H, HC=CH); 4.13 (*qa*, *J* = 7, 2 H, CH_2–O); 2.90–1.75 (*m*, 10 H, 5 CH_2); 1.23 (*t*, *J* = 7, 3 H, CH_3); 0.92 (*t*, *J* = 7.5, 3 H, CH_3). – MS.: 212 (*M*, 11), 101 (100), 98 (68), 55 (66), 137 (64), 69 (62), 68 (62), 41 (59), 145 (49).

(Z)-*γ-Jasmolactone* (**2**). (*Z*)-4-Oxo-dec-7-enoic acid ethylester (**14**) (31.9 g, 0.15 mol) in 100 ml ethanol was added dropwise to a cooled (0°) and stirred solution of $NaBH_4$ (3.8 g, 0.1 mol) and Na_2HPO_4 (22 g, 0.124 mol) in 150 ml water. The reaction mixture was left at RT. for 15 h. A large excess of 2N NaOH was added, and after 15 min, the mixture was extracted with ether. The aqueous phase was acidified with an excess of conc. hydrochloric acid and extracted 3 times with ether. The organic layers were washed twice with brine, and dried (Na_2SO_4). The solvent was evaporated at 40°/11 Torr and the oily, crude product was distilled through a *Vigreux*-column, whereby 14.3 g (65%) of pure (GC.) (*Z*)-γ-jasmolacetone (**2**)

were obtained. – IR. (liq.): 1780, 1460, 1355, 1050, 970, 910, 900. – ^{1}H-NMR.: 5.70–5.00 (*m*, 2 H, HC=CH); 4.50 (*qi*, *J* = 6.5, 1H, CH–O); 2.75–1.45 (*m*, 10 H, 5 CH_2); 0.95 (*t*, *J* = 7.5, 3 H, CH_3). – MS.: 168 (*M*, 4), 68 (100), 85 (35), 41 (24), 29 (22), 55 (18), 108 (10), 95 (9), 150 (4).

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