86. Isolation and Total Synthesis of (*E*)-6,10-Dimethyl-9-methylidene-undec-5-en-2-one, a Constituent of Costus Root Oil

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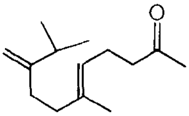
Summary

(*E*)-6,10-Dimethyl-9-methylidene-undec-5-en-2-one (**1**) has been isolated from *Costus* root oil. A total synthesis of this compound is reported.

Analysis. - A recent communication [1] on the isolation of **1** from *Costus* root oil and its partial synthesis prompts us to give an account of our own findings in this field.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The essential oil obtained by steam distillation of dried *Costus* roots (*Saussurea lappa* CLARKE)[1]) is much appreciated as an expensive perfumery raw material [2]. It displays a long lasting odour of a fatty, woody and very pronounced animal character. *Costus* oil finds use in oriental-, certain floral- and aldehydic-type fragrances. Since 1914 [3] *Costus* oil has been the subject of several [4] analytical investigations.

From the ionone-fraction of the above oil[2]) the following constituents were among those isolated and characterized:

α- and β-ionone (*Naves* [5]),
dihydro-α-ionone (**2**) and (*E*)-geranylacetone (**3**) (new in *Costus* oil),
(*E*)-6,10-dimethyl-9-methylidene-undec-5-en-2-one (**1**).

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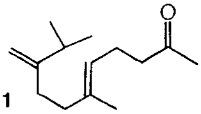

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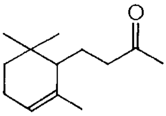

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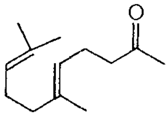

The ¹H-NMR., IR. and mass spectra of compound **1** are in good agreement with the literature [1]. The ^{13}C-NMR.-values of **1** compared with the depicted values of the structurally closely related (*E*)- and (*Z*)-geranylacetones (**3**) and (**4**) support the proposed (*E*)-configuration [6].

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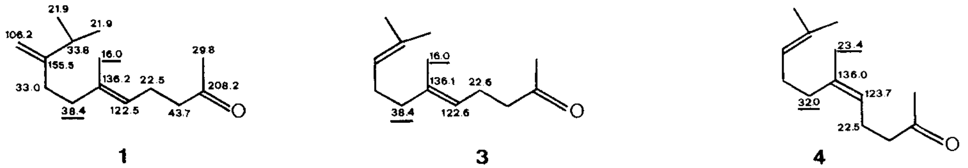
[1]) *Saussurea lappa* is a member of the *Compositae* family growing wild in the *Himalayan* highlands.

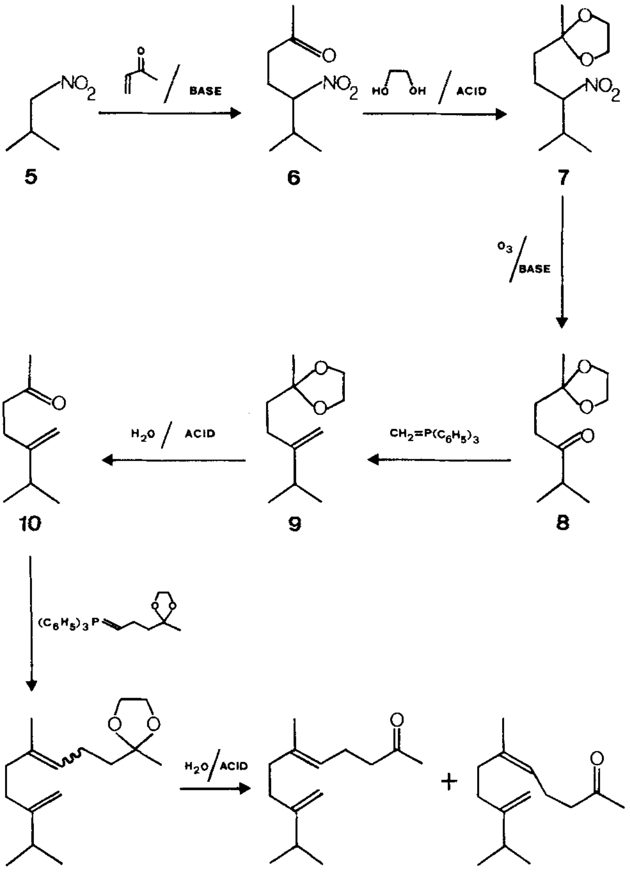
[2]) Origin of commercial sample: *Payan & Bertrand*, Grasse.

^{13}C-NMR.-assignments[3])



1 **3** **4**

Scheme 1. *Total synthesis of* **1**



1-Nitro-2-methyl-propane (**5**) was prepared from isobutyl iodide by treatment with sodium nitrite in dimethyl sulfoxide (*cf.* [7]). Condensation of **5** with methyl vinyl ketone in methanol, in the presence of catalytic amounts of sodium methanolate, gave γ-nitroketone **6**. The keto function of **6** was protected by

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[3]) $CDCl_3$; ppm values relative to internal TMS = 0. Off-resonance-decouplings: Irradiation at 400 Hz upfield TMS. Noise-bandwidth: 1000 Hz.

conversion to the corresponding 1,3-dioxolane **7**. Ozonisation of the deprotonated nitro-compound **7** under the conditions described by *McMurry* [8] proved to be by far the best way[4] to obtain the monoprotected diketone **8**. *Wittig* reaction of **8** with methylidene-triphenyl-phosphorane in dimethyl sulfoxide [11] afforded the desired acetal **9**. Removal of the protecting group of **9** gave *thuja ketone* **10** [12], subsequently converted to a mixture of (*E*)- and (*Z*)-**11** under the *Wittig* conditions described by *McMorris* [13]. The stereoisomeric mixture of **11** was deacetalized in aqueous monoglyme in the presence of catalytic amounts of *p*-toluenesulfonic acid to give a mixture of (*E*)- and (*Z*)-**1** (60:40), separated by preparative GC. The more abundant stereoisomer (*E*)-**1** showed the same IR., ^{1}H-NMR., ^{13}C-NMR. and mass spectra, GC. (longer retention times on both polar and apolar columns than for minor stereoisomer ((*Z*)-**1**) and olfactive properties as (*E*)-6,10-dimethyl-9-methylidene-undec-5-en-2-one from *Costus* root oil.

The authors are indebted to Dr. *E. Billeter*, Mr. *J. Maerki* and Mrs. *A. Kappeler* for their NMR. services and to Dr. *P. Schudel* for his encouragement. The analytical part of the work was carried out with the aid of Miss *R. Foschi*, Mr. *H. Aeppli* and Mr. *W. Scherrer*. The help of Mrs. *E. Trutmann* during the synthesis is gratefully acknowledged.

Experimental Part

General. - NMR. spectra were recorded on a *Varian* XL-100 A instrument (100 MHz for ^{1}H-NMR. and 25.2 MHz for ^{13}C-NMR.), in $CDCl_3$ with TMS (0 ppm) as internal standard; abbreviations: *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quartet, *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. Isolation of naturally occurring material. - Distillation of a commercial sample of *Costus* oil[2] on a *Widmer*-column (length: 30 cm) yielded a fraction (4.1% of total oil; b.p. 72-84°/0.05 Torr) containing **1**. Chromatography on a 15-fold amount of silica gel (*Merck*, 0.05-0.2 mm) with hexane → hexane/ether 5:1 gave a fraction (0.82% of total oil) containing mainly dihydro-α-ionone (**2**), (*E*)-geranylacetone (**3**), α- and β-ionones as well as **1**. Rechromatography of the above fraction on a 30-fold amount of silica gel (*Merck*, 0.05-0.2 mm) with hexane/ether 10:1 and prep. GC. (Carbowax 20 M) of the first eluate (0.09% of total oil) yielded compound **1** (0.04% of total oil), dihydro-α-ionone (**2**), and (*E*)-geranylacetone (**3**) which all were shown to be single isomers by capillary-GC.[5]. The last eluates of this chromatography contained α- and β-ionones (GC./MS.).

(E)-6,10-Dimethyl-9-methylidene-undec-5-en-2-one (**1**): IR. (liq.): 3080, 1715, 1645, 900. - ^{1}H-NMR.: 5.09 (br. *t*, *J* = 6.5, 1 H, $CH{=}C$); 4.73 (br. *s*, 1 H, from $CH_2{=}C$); 4.66 (br. *s*, 1 H, from $CH_2{=}C$); 2.60-2.18 (br. *m*, 5 H); 2.15 *s*, 3 H, $CH_3{-}CO$); 2.10 (br. *s*, 4 H); 1.63 (br. *s*, 3 H, $CH_3{-}C{=}$); 1.03 (*d*, *J* = 6.5, 6 H, 2 $H_3C{-}C(10)$). - MS.: 208 (*M*, < 1), 43 (100), 107 (44), 150 (38), 135 (18), 81 (18), 123 (17), 55 (17), 95 (13).

Dihydro-α-ionone (**2**): IR. (liq.): 3030, 1715. - ^{1}H-NMR.: 5.43 (br. *m*, 1H, $CH{=}C$); 2.70-2.15 (br. *m*, 2 H); 2.13 (*s*, 3 H, $CH_3{-}CO$); 2.10-1.00 (br., 7 H); 1.68 (*m*, 3 H, $CH_3{-}C{=}$); 0.93 (*s*, 3 H,

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[4] Other, less successful oxidation conditions for **7** → **8**: a) 30% hydrogen peroxide (approx. 6 mol-eq.)/aqueous sodium hydroxide (1.2 mol-eq.)/methanol/ambient or reflux temperature; b) *t*-butyl hydroperoxide/vanadyl acetylacetonate/potassium *t*-butanolate/*t*-butanol [9]; c) potassium permanganate/magnesium sulfate/potassium hydroxide [10].

[5] Ucon HB 5100, 50 m × 0.31 mm; *H. & G. Jaeggi*, Labor für Gaschromatographie, CH-9043 Trogen.

$CH_3-C(1)$); 0.88 (*s*, 3 H, $CH_3-C(1)$). - MS.: 194 (*M*, 1), 43 (100), 95 (46), 121 (42), 136 (36), 81 (28), 93 (28), 91 (22), 79 (19). - $[\alpha]_D^{20}$: +63.40° (c=0.870, $CHCl_3$)[6].

2. Synthesis of (*E*)-6,10-dimethyl-9-methylidene-undec-5-en-2-one (1). - *1-Nitro-2-methyl-propane* (**5**). Following [7], isobutyl iodide (36.8 g, 0.20 mol) reacted with sodium nitrite (24,15 g, 0.35 mol) in 150 ml dimethyl sulfoxide. The ethereal extract was concentrated through a small column and the residual liquid rectified through a *Widmer*-column at 40 Torr. 10.38 g (50.4%) of pure 1-nitro-2-methyl-propane (**5**), b.p. 56-58°/40 Torr, n_D^{20}= 1.4075[7]), were obtained as colourless liquid. - IR. (liq.): 1555, 1470, 1385, 1230. - ^{1}H-NMR.: 4.20 (*d*, J=7, 2 H, CH_2-NO_2); 2.47 (*nonuplet*, J=7, 1H, CH); 1.02 (*d*, J=7, 6 H, $2 H_3C-C(2)$). - MS.: 103 (*M*, < 1), 41 (100), 57 (76), 39 (36), 56 (23), 55 (14), 43 (13), 42 (11), 40 (6).

$C_4H_9NO_2$ (103.12) Calc. C 46.59 H 8.80 N 13.58% Found C 46.27 H 8.62 N 13.30%

6-Methyl-5-nitro-heptan-2-one (**6**). To a vigorously stirred solution of methyl vinyl ketone (35 g, 0.50 mol) and 1-nitro-2-methyl-propane (**5**) (51.5 g, 0.50 mol) in 450 ml methanol, solid sodium methanolate (1.0 g, 0.019 mol) was added. Stirring was continued for 2 h at 40° under argon. The solvent was removed by evaporation at 11 Torr, and the residue diluted with 200 ml ether and 200 ml saturated $NaHCO_3$-solution. The aqueous phase was extracted with ether (3×200 ml). The combined extracts were washed with 150 ml of brine and dried (Na_2SO_4). After evaporation of the solvent at 11 Torr the residue was fractionally distilled over a 10 cm *Vigreux*-column at 0.04 Torr, when 53.85 g (62.3%) pure 6-methyl-5-nitro-heptan-2-one (**6**), b.p. 76°/0.04 Torr (n_D^{20}= 1.4443) were obtained as colourless liquid. - IR. (liq.): 1725, 1550, 1370, 1170. - ^{1}H-NMR.: 4.25 (*qa*, J=6, 1H, $HC-NO_2$); 2.70-1.75 (br., 5 H, CH_2-CH_2-HC); 2.15 (*s*, 3 H, CH_3-CO); 0.98 (*d*, J=7, 3 H, $H_3C-C(6)$); 1.05 (*d*, J=7, 3 H, $H_3C-C(6)$). - MS.: 173 (*M*, 0), 43 (100), 69 (32), 41 (22), 55 (13), 109 (11), 83 (7), 39 (6), 71 (6).

$C_8H_{15}NO_3$ (173.21) Calc. C 55.47 H 8.73 N 8.09% Found C 55.62 H 8.79 N 8.10%

Dioxolane **7**. A solution of **6** (50 g, 0.29 mol), ethyleneglycol (35.9 g, 0.58 mol), *p*-toluenesulfonic acid (0.95 g) in 650 ml benzene was heated at reflux for 15 h under azeotropic removal of water. The solvent was evaporated at 11 Torr and the residual liquid diluted with 200 ml ether and 150 ml saturated aq. Na_2CO_3-solution. The aqueous phase was extracted with ether (3×200 ml). The combined organic phases were washed with 150 ml of brine and dried (Na_2SO_4). After removal of the solvent at 11 Torr the resulting liquid was rectified through a 10 cm *Vigreux*-column at 0.05 Torr, when 58.8 g (93.8%) of pure dioxolane **7**, b.p. 95-96°/0.05 Torr, n_D^{20}= 1.4519, were obtained as a colourless oil. - IR. (liq.): 1550, 1370, 1250, 1040, 945, 850. - ^{1}H-NMR.: 4.27 (*qa*, J=6, 1H, $HC-NO_2$); 3.90 (*s*, 4 H, $O-CH_2-CH_2-O$); 2.40-1.40 (br., 5 H, CH_2CH_2-CH); 1.30 (*s*, 3 H, $CH_3-C(2)$); 1.00 (*d*, J=7, 3 H, $H_3C-C(6)$); 0.95 (*d*, J=7, 3 H, $H_3C-C(6)$). - MS.: 217 (*M*, 0), 87 (100), 43 (48), 69 (20), 41 (13), 202 (11), 99 (10), 109 (8), 55 (6).

$C_{10}H_{19}NO_4$ (217.26) Calc. C 55.28 H 8.82 N 6.45% Found C 55.43 H 8.60 N 6.52%

Acetal **8**. To a solution of dioxolane **7** (10 g, 46.08 mmol) in 100 ml methanol, was added NaOH (3.7 g, 92.5 mmol) dissolved in 25 ml water, and the mixture subsequently cooled to −78° with dry ice/acetone. After ozonisation at −78° the reaction mixture was first purged with O_2 and then with a stream of argon, and the temperature was raised to −30°. The reaction mixture was then poured into 100 ml of 10% aq. NaHSO-solution the aqueous phase was extracted at 0° with ether (3×200 ml). The extracts were washed with saturated aq. $NaHCO_3$-solution, then with brine, combined, and dried (Na_2SO_4). The solvent was evaporated at 11 Torr and the resulting residue was distilled through a *Widmer*-column at 0.04 Torr. 6.37 g (74.2%) of pure **8**, b.p. 63°/0.04 Torr, n_D^{20}= 1.4422, were obtained as colourless oil. - IR. (liq.): 1710, 1470, 1380, 1255, 1220, 1140, 1080, 950, 860. - ^{1}H-NMR.: 3.98 (*s*, 4 H, $O-CH_2-CH_2-O$); 2.95-2.40 (br., 3 H, $CH_2-CO-CH$); 2.20-1.80 (*m*, 2 H, $2 H-C(3)$); 1.35 (*s*, 3 H, $3 H-C(1)$); 1.12 (*d*, J=7, 6 H, $2 H_3C-C(6)$). - MS.: 186 (*M*, 0), 87 (100), 43 (74), 99 (28), 71 (14), 143 (11), 171 (9), 41 (9), 55 (6).

$C_{10}H_{18}O_3$ (186.25) Calc. C 64.49 H 9.74% Found C 64.45 H 9.67%

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6) $[\alpha]_D^{20}$= + 160° [14]; + 167° [5].

7) Lit. [15]: n_D^{20}= 1.4069.

2,2-Ethylenedioxy-6-methyl-5-methylideneheptane (**9**). Sodium hydride (2.22 g, 52.4 mmol, 57% dispersion in oil) in a 200 ml three-necked flask, fitted with a magnetic stirrer, was washed as usual and the system filled with argon. Abs. dimethyl sulfoxide (25 ml) was then introduced, and the mixture was heated at 75-80° for 45 min, when the evolution of H_2 had ceased. The resulting solution of methylsulfinyl carbanion was cooled in an ice-water bath, and methyltriphenylphosphonium bromide [16] (18.7 g, 52.4 mmol) in 55 ml of warm dimethyl sulfoxide was added. The resulting dark red solution of methylidene-triphenyl-phosphorane was stirred at RT. for 10 min before **8** (7.8 g, 42 mmol), in 30 ml of dimethyl sulfoxide, was added. The temperature rose to 40° during addition; the reaction mixture was then heated at 60° for 3 h. The solution was cooled and poured into 100 ml of water, whereby triphenyl phosphine oxide was precipitated. This mixture was extracted with pentane (4× 150 ml). The pentane fractions were combined and washed with 100 ml of water/dimethyl sulfoxide 1:1, then with 150 ml of brine. The pentane layer was dried (Na_2SO_4), the solvent was distilled off at normal pressure and the resulting liquid residue was distilled through a *Vigreux*-column at 11 Torr. 6.35 g (82.5%) of pure **9**, b.p. 88-90°/11 Torr, $n_D^{20} = 1.4472$, were obtained as colourless oil. - IR. (liq.): 3090, 1645, 1460, 1375, 1250, 1220, 1130, 1050, 945, 890, 865. - ^{1}H-NMR.: 4.70 (*m*, 2 H, $CH_2{=}C$); 3.92 (*s*, 4 H, $O{-}CH_2{-}CH_2{-}O$); 2.50-1.55 (br., 5 H, $CH_2{-}CH_2{-}CH$); 1.32 (*s*, 3 H, 3 H−C(1)); 1.02 (*d*, *J* = 7, 6 H, 2 CH_3−C(6)). - MS.: 184 (*M*, 0), 87 (100), 43 (38), 41 (10), 55 (8), 81 (5), 39 (5), 99 (4), 107 (4).

$C_{11}H_{20}O_2$ (184.28) Calc. C 71.70 H 10.94% Found C 71.84 H 10.94%

6-Methyl-5-methylideneheptan-2-one (**10**). 4.5 g (24.5 mmol) **9**, dissolved in a mixture of 45 ml 1,2-dimethoxyethane, 9 ml of water and 0.2 g of *p*-toluenesulfonic acid, was heated at reflux for 2 h in an argon atmosphere. The reaction mixture was diluted with 100 ml of saturated aq. $NaHCO_3$-solution and extracted with ether (3× 100 ml). The organic phases were twice washed with small amounts of brine, combined, and dried (Na_2SO_4). The solvent was removed by distillation at normal pressure and the residual liquid rectified through a 7 cm *Vigreux*-column at 11 Torr to obtain 2.69 g (78.7%) of pure **10**, b.p. 60-62°/11 Torr[8]) ($n_D^{20} = 1.4385$), as a colourless liquid. - IR. (liq.): 3100, 1720, 1645, 1465, 1420, 1360, 1155, 890. - ^{1}H-NMR.: 4.76 (*m*, 1H, from $CH_2{=}C$); 4.62 (*m*, 1H, from $CH_2{=}C$); 3.82-1.95 (br., 5 H, $CH_2{-}CH_2{-}CH$); 2.15 (*s*, 3 H, $CH_3{-}CO$); 1.02 (*d*, *J* = 7, 6 H, 2 H_3C−C(6)). - MS.: 140 (*M*, < 1), 43 (100), 55 (49), 41 (39), 39 (27), 67 (15), 69 (12), 53 (11), 83 (9), 97 (9), 122 (9).

$C_9H_{16}O$ (140.23) Calc. C 77.09 H 11.50% Found C 76.64 H 11.36%

(E)+(Z)-2,2-Ethylenedioxy-6,10-dimethyl-9-methylidene-undec-5-ene ((*E*)-+(*Z*)-**11**). (4,4-Ethylenedioxy)pentyltriphenylphosphonium iodide [17][9]) (42.7 g, 82.4 mmol) were suspended in 260 ml of abs. benzene; subsequently 47.12 ml of a solution of sodium *t*-amylate in benzene (1.75M) [18] was added under argon, and then 6-methyl-5-methylideneheptan-2-one (**10**) (9.24 g, 66 mmol) dissolved in 130 ml of benzene were introduced dropwise. The combined solution was refluxed for 24 h, cooled and filtered from the precipitated triphenylphosphine oxide. The resulting mixture was poured into water and extracted with pentane (3× 200 ml). The organic phases were washed with 3× 100 ml of brine, combined, dried (Na_2SO_4), and concentrated at 11 Torr. The liquid residue was distilled through a 5 cm *Widmer*-column at 0.06 Torr. 7.0 g (42.1%) of a mixture of (*E*)- and (*Z*)-**11** *ca.* 60:40 (GC.) were obtained as colourless liquid. B.p. 98-100°/0.06 Torr. - IR. (liq.): 3100, 1650, 1455, 1380, 1260, 1220, 1140, 1060, 955, 895, 870. - ^{1}H-NMR.: 5.15 (br. *t*, *J* = 7, 1H, CH−C=); 4.73 (br., 2 H, $CH_2{=}C$); 3.95 (*s*, 4 H, $O{-}CH_2{-}CH_2{-}O$); 2.12 (br. *s*, 6 H); 1.90-1.40 (*m*, 6 H); 1.33 (*s*, 3 H, H_3C−C(2)); 1.05 (*d*, *J* = 7, 6 H, 2 H_3C−C(6)). - MS.: 252 (*M*, 4), 150 (100), 43 (88), 87 (71), 107 (48), 147 (29), 41 (28), 190 (22), 115 (21).

$C_9H_{28}O_2$ (252.40) Calc. C 76.14 H 11.18% Found C 76.55 H 11.39%

(E)-+(Z)-6,10-Dimethyl-9-methylidene-undec-5-en-2-one (*E*)-+(*Z*)-(**1**). The previous (*E*)- and (*Z*)-mixture of dioxolane **11** (3.12 g, 12.4 mmol), dissolved in a mixture of 30 ml 1,2-dimethoxyethane, 6.2 ml of water and 0.3 g of *p*-toluenesulfonic acid, was heated at reflux for 2 h under argon. The reaction mixture was diluted with 100 ml of saturated aq. $NaHCO_3$-solution and extracted with 3× 100 ml ether. The organic phases were twice washed with small quantities of brine, combined, and dried (Na_2SO_4). The solvent was evaporated, and the remaining liquid was distilled *in vacuo* through a short *Vigreux*-column. 2.11 g (83%) of a

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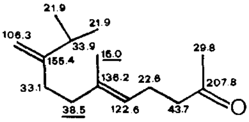
[8]) Lit. [12]: b.p. 73-76°/15 Torr.

[9]) We thank Dr. *G. Fráter* (*Socar*, Dübendorf) for larger amounts of this reagent.

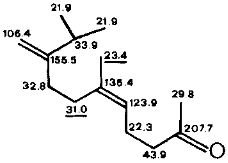
pure mixture of (*E*)- and (*Z*)-**1** *ca.* 60:40, b.p. 66-80°/0.05 Torr, were obtained as a colourless liquid. A sample of the mixture of (*E*)-**1** and (*Z*)-**1** yielded pure (*E*)-**1** and pure (*Z*)-**1** by GC.

(*E*)-**1**: IR. and ^{1}H-NMR. spectra identical with that of natural (*E*)-**1**. - MS.: 208 (*M*, 2), 107 (100), 150 (97), 43 (77), 123 (49), 135 (41), 41 (39), 81 (32), 55 (31).
^{13}C-NMR. (shifts and assignments):



$C_{14}H_{24}O$ (208.34) Calc. C 80.71 H 11.61% Found C 80.87 H 11.85%

(*Z*)-**1**: IR. ($CHCl_3$): 1715, 1645, 1070, 1035, 900. - ^{1}H-NMR.: 5.11 (br. *t*, *J* = 6.5, 1 H, CH=C); 4.78 (br. *s*, 1 H, from CH_2=C); 4.72 (br. *s*, 1 H, from CH_2=C); 2.57-2.17 (br. *m*, 5 H); 2,15 (br. *s*, 7 H); 2.11 (*d*, *J* = 1.5, 3 H, CH_3-C=); 1.06 (*d*, *J* = 6.5, 6 H, 2 H_3C-C(6)). - MS.: 208 (*M*, 2), 107 (100), 150 (88), 43 (72), 123 (50), 135 (40), 41 (40), 81 (37), 55 (30).
^{13}C-NMR. (shifts and assignments):



$C_{14}H_{24}O$ (208.34) Calc. C 80.71 H 11.61% Found C 80.19 H 11.70%

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