38. On the Stereochemistry of the Irones

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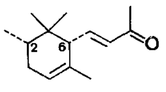
(14.XI.83)

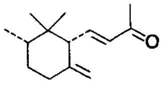
Summary

In view of the demonstration by *Jaenicke et al.* that different *Iris* varieties produce enantiomeric irones [6], we complement our 1971 paper on the stereochemistry of the irones [3]. *1)* We give what information we have on the origin of the *Iris* oil used in [3]; *2)* we show that we and *Ruzicka et al.* on whose degradation work our determination of the C(2)-configurations was based had the same irones in hand; *3)* we summarize independent assignments of the C(2)-configurations and the relative configurations of the *α*-irones. *4)* We also describe the identification of a trace of the 'missing' *trans-γ*-irone in our oil, and *5)* revise the preferred conformation of the *cis-α*-irones in solution.

After having identified the long-sought natural precursors of the irones [1], *Jaenicke*'s group has now found that chemical degradation of the precursors they isolated gives (−)-(2*S*,6*R*)-*cis-α*-irone¹) ((2*S*,6*R*)-**1**) and (−)-(2*S*,6*R*)-*cis-γ*-irone ((2*S*, 6*R*)-**2**) and demonstrated that different *Iris* varieties produce enantiomeric precursors and irones [6]. In particular it turns out that the irones we had in hand when we established the relative and absolute configurations in 1971 [3] were the enantiomers of *Jaenicke*'s. We wish to complement our 1971 paper; these findings demand precisions, and new data of our own and from other groups have accumulated.



(−)-(2*S*,6*R*)-1



(−)-(2*S*,6*R*)-2

1. Origin of the *Iris* Oil Used in [3]. – Unfortunately, we do not know the origin of our 'Essence Absolue *Iris*'. It was probably purchased from *Roure Bertrand Dupont*, Grasse, well before 1968 and, if so, the rhizomes were probably of *Iris pallida*²) cultivated in Italy [7].

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¹) Numbering of the C-atoms according to the *IUPAC* tentative rules for the nomenclature of carotenoids [2], different from that used in [3] [4] and [5].

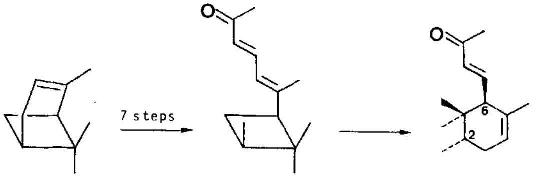
²) We thank Dr. *C. Ehret, Roure Bertrand Dupont SA*, Grasse, for his help in our attempts to trace the origin of our oil.

2. *Ruzicka's* Irones. – Our assignments of the relative configurations [3] were based on independent determinations of the absolute configurations at both chiral centers, and our assignments of the C(2)-configurations were based on an oxidative degradation of *cis-γ*-irone (**2**) carried out by *Ruzicka*'s group in the 1940's. Our assignments of the C(2)-configurations and the relative configurations would be in error if *Ruzicka* had had the enantiomers of our irones in hand, but we know that *Ruzicka* had the same irones as we: in 1970, we obtained^{3}) samples of irones^{4}) that had been distilled in *Ruzicka*'s laboratory in 1950 from which we isolated^{4}) (+)-**1** ($[\alpha]_D^{20} = +55°$ (CH_2Cl_2, $c = 0.879$)) and (+)-**2** ($[\alpha]_D^{20} = +2°$ (CH_2Cl_2, $c = 0.443$)).

3. Independent Assignments. – Two independent correlations are in accord with our assignments [3] of the C(2)-configurations.

In an unpublished study carried out in parallel with [3] we synthesized (+)-(2*S*,6*S*)-*trans-α*-irone ((2*S*,6*S*)-**3**) from (–)-(1*S*, 5*S*)-*α*-pinene ((1*S*,5*S*)-**4**) in low yield by a variant of *Eschinazi*'s synthesis [10]. (1*S*,5*S*)-**4** ($[\alpha]_D^{20} = -43.75°$ (neat), 85% optically pure [11]) was transformed into (*E*,*E*,1′*S*,3′*S*)-6-(2′,2′,3′-trimethylcyclobutyl)-3,5-heptadien-2-one ((*E*,*E*,1′*S*,3′*S*)-**5**) (see *Scheme 1* and *Exper. Part*) by a seven-step sequence: ozonolysis and reduction, decarbonylation [12], ethynylation [13], etherification and *Claisen* rearrangement [14], isomerization with NaOH [14], and photochemical isomerization. Thermolysis of (*E*,*E*,1′*S*,3′*S*)-**5** in a quartz tube at *ca.* 310° and atmospheric pressure afforded a mixture of products from which (2*S*,6*S*)-**3** of 73% optical purity [3] ($[\alpha]_D^{20} = +306°$ (CCl_4, $c = 0.980$)), which corresponds to 86% of the optical purity of the starting material (1*S*,5*S*)-**4**, was isolated. The vinylcyclobutane-cyclohexene rear-

Scheme 1



(–)-(1*S*,5*S*)-**4** (*E*,*E*,1′*S*,3′*S*)-**5** (+)-(2*S*,6*S*)-**3**

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3) From *D. Felix* and *A. Eschenmoser*.

4) 'Fraktionen 17, 18, 21, 22, zweite Destillation an der *Podbielniak*-Kolonne, 17.3.1950.' (+)-**1** ($[\alpha]_D^{20} = +55°$) was isolated by GC from 'Fraktion 17' which consisted of about 95% of (+)-**1** and 5% of **2** as determined by GC analysis. (+)-**2** ($[\alpha]_D^{20} = +2°$) was isolated from 'Fraktion 22' which consisted of about 90% of (+)-**2** and 10% of **1**. (We reported this $[\alpha]_D^{20}$-measurement in [3] because this sample was of somewhat higher chemical purity than those isolated from our own oil. Both sources contained virtually optically pure (+)-**2**.) 'Fraktionen 17, 18, 21, 22' must come from the distillation reported in [8] which gives an $\alpha_D = +49°$ for an irone obtained from 'Fraktion 17' by purification with *Girard* reagent and correctly identified as (+)-**1**. *Ruzicka* [8] also located and identified (+)-**2** correctly but 'Fraktion 21' which by our GC analysis consisted of about 75% of **1** and 25% of **2** – the next 'Fraktion 22' was much purer (see above) – was chosen for purification *via* the phenylsemicarbazone which gave two samples with $\alpha_D = +13.7°$ and $+5.7°$. The same paper [8] also correctly identifies (+)-*trans*-irone ((+)-**3**) with $\alpha_D = +327°$. The origin of the oil that was used is not given, but [9] specifies: *Iris florentina* roots and *Iris concrète* from *Roure-Bertrand*, Fils, Grasse.

rangement [15] (*E*,*E*,1′*S*,3′*S*)-**5**→(2*S*,6*S*)-**3**, a [1,3]-sigmatropic shift, leaves the chiral integrity of the center that becomes C(2) in (2*S*,6*S*)-**3** largely intact and thus establishes the (2*S*)-configuration of (+)-**3**.

Two further components of the mixture, namely *cis*-*a*-irone (**1**) (**1**/**3** = *ca.* 2:7) and 1-(4-methyl-1,3-cyclohexadienyl)-1-ethanone (**6**), were identified. Rough estimates for the yields of these components in the mixture are 10–20% for **1** + **3** and 30–40% for **6**. The latter is formed by cleavage, electrocyclization, and a [1,5]-H shift.

In addition, *Yoshikoshi*'s group has since reported a synthesis of (−)-(2*R*,6*R*)-**3** starting from (+)-(*R*)-citronellal [4][5]) which independently establishes the (2*R*)-configuration of (−)-**3**.

Finally, *Steinmetz*'s assignments of the relative configurations of the *a*-irones in the gas phase by low-resolution microwave spectroscopy [17] are in accord with ours [3].

4. The Missing γ-Irone.

– We were struck by the fact that our oil [3] contained both the *cis*-α-irone (2*R*,6*S*)-**1** and the *trans*-*a*-irone (2*S*,6*S*)-**3**, but only a single γ-irone, the *cis*-γ-irone (2*R*,6*S*)-**2**. The missing *trans*-γ-irone (**7**) was also not detected in our isomerization experiments [3] and in *Jaenicke*'s chemical degradation work [1] [6]. Two syntheses of its racemate ((2*RS*,6*RS*)-**7**) [5] [16] and one of (+)-(2*R*,6*R*)-**7** (*Yoshikoshi*'s precursor of (2*R*,6*R*)-**3** [4]) have since been reported. A sample of (2*RS*,6*RS*)-**7** kindly furnished by Professor *K. Mori* [16] has now enabled us to identify a trace of **7** in our oil by GC/MS coupling[6]).

5. Conformations of the α-Irones.

– We had deduced from the CD spectra that the preferred conformations of the *cis*-*a*-irones (**1**), *trans*-*a*-irones (**3**), and *a*-ionones (**8**) in solution are half chairs with the side chain pseudoaxial [3] [18]. By 360-MHz ^{1}H- and 90.55-MHz ^{13}C-NMR spectroscopy we have since confirmed this for **3** and **8** but have found that **1** has a pseudoequatorial side chain. On double irradiation at the frequency of the C(2)−CH_3 *d*, the 360-MHz ^{1}H-NMR spectrum[7]) of **1** in $CDCl_3$-solution (TMS as standard) shows the C(2)−H signal as a *dd* with coupling constants of 5.5 and 11.0 Hz centered at 1.49 ppm. This proves that the C(2)−H is axial. Hence the C(2)−CH_3 must be equatorial and the side chain pseudoequatorial. This pattern could not be observed directly for **3**[7]) because the C(2)−H signal and one of the C(3)−H signals have very similar chemical shifts but on Eu(fod)$_3$-complexation ($CDCl_3$) virtually the same *dd* was seen. Hence the C(2)−CH_3 must again be equatorial and the side chain now pseudoaxial.

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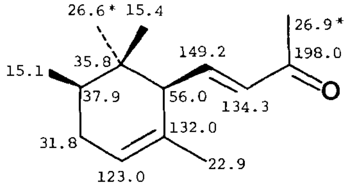
[5]) *Yoshikoshi et al.* erroneously state [4] that we [3] showed that our irones all had the (2*R*)-configuration[1]). In fact our irones all had the (6*S*)-configuration[1]) [3]. This error seems to have found its way into [16].

[6]) In addition, traces of three further isomers were seen, one of which must be a (*Z*)-α-irone.

[7]) The key experiments were done using $CDCl_3$-solutions but ^{1}H-NMR spectra of **1** and **3** in CD_3CN-, C_6D_6- and $C_6D_5CD_3$-solutions were also recorded. In both cases, the preferred conformations in these solvents clearly were the same. Low-temperature (203 K) studies kindly carried out by *U. Burger*, University of Geneva, showed no significant changes. *G. Snatzke*, Ruhr Universität Bochum, kindly measured the CD spectra of (+)-**1** and (+)-**3** in CH_3CN-solution and these did not differ significantly from our earlier spectra [3] [18]. Thus we observe the same conformers by CD and NMR.



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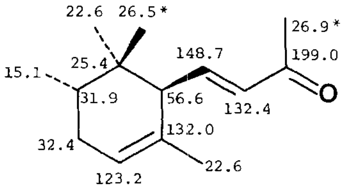

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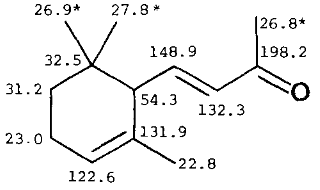

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*chemical shifts may be interchanged

Our assignments of the ^{13}C-resonances of **1**, **3** and **8** in $CDCl_3$-solution (TMS as standard) are given above. The pseudoaxial side chain in **3** and **8** induces a strong *γ-gauche* effect on C(2) and this effect is absent in the case of **1**.

This reassignment, which is in accord with *Steinmetz*'s assignment in the gase phase [17], does not change the argument in [18] because the pseudoaxial and the pseudo-equatorial side chain will lead to a CD couplet of the same sign [19].

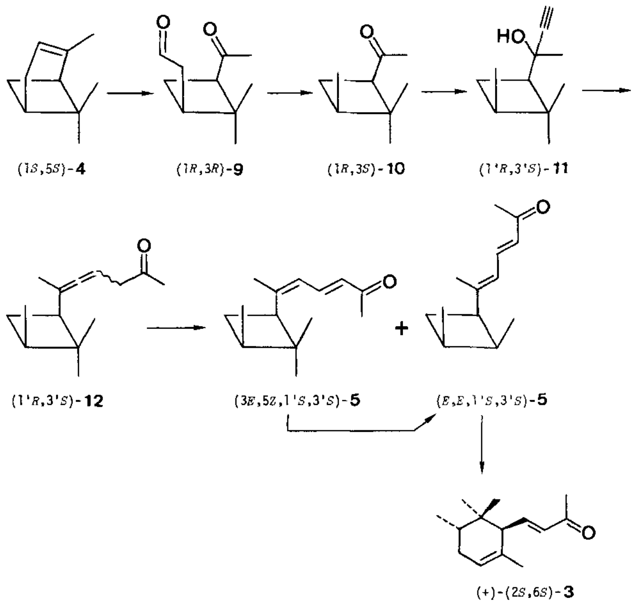
Experimental Part

1. ***Ruzicka*'s Irones.** – Samples were isolated by GC as described in [3]. Specific rotations were measured with a *Perkin-Elmer 141* polarimeter.

2. **(2*S*,6*S*)-3 from (1*S*, 5*S*)-4** (see *Scheme 2*). – Specific rotations were measured in CCl_4 with a *Perkin-Elmer 141* polarimeter. GC was performed on *F&M 500* and *Carlo Erba GT* instruments using regular *Carbowax 20 M 15* columns. IR spectra of neat films were recorded on a *Perkin-Elmer 125* instrument; characteristic bands are given in cm^{-1}. 60-MHz ^{1}H-NMR spectra were measured on *Varian A 60* and *Hitachi Perkin-Elmer R-20B* spectrometers using CCl_4 as the solvent. Chemical shifts are expressed in ppm (δ-scale) downfield from TMS as an internal standard; abbreviations: *s* = singlet, *d* = doublet, *dd* = doublet of doublets, *t* = triplet, *m* = one or several overlapping multiplets, br. = broad, *J* = spin-spin coupling constant (Hz). Mass spectra were recorded on an *Atlas CH4* mass spectrometer using an inlet temperature of *ca.* 150° and electrons of *ca.* 70 eV energy; the intensity of the molecular ion (M^+) and of 5–7 of the most intense fragment ions are given in % of the most abundant fragment ion. Distilled products were usually of *ca.* 95% purity (GC). Analytical samples were purified to ≥98% purity by preparative GC.

2.1. *(1*R*,3*R*)-3-Acetyl-2,2-dimethylcyclobutaneacetaldehyde ((1*R*,3*R*)-**9**).* Ozone was bubbled through a cooled (–10°) solution of 50.0 g of (–)-(1*S*,5*S*)-**4** (0.37 mol), $a_D^{20} = -37.43°$ (neat, l = 1 dm), in 500 ml of CH_2Cl_2 and 500 ml of AcOH until aq. KI in a bubbler fitted to the O_2 outlet turned dark-brown (20 h). After purging with N_2, 58.0 g of dimethyl sulfide (0.93 mol) was added dropwise (20 min) to the cooled (–10°) mixture. Stirring was continued for 1 h at –10°, then for 1 h at 3° and then for 1 h at r.t. The mixture was then poured into H_2O. Extraction, drying, removal of the solvents, and distillation afforded 28.0 g of (1*R*,3*R*)-**9** (44%), b.p. 73–74°/0.01 Torr, $[\alpha]_D^{20} = -67.4°$ (*c* = 1.08). IR: 1700, 1720. ^{1}H-NMR: 0.82, 1.32 (*s*, 3H each); 1.70–2.60 (*m*, 5H); 1.98 (*s*, 3H); 2.92 (*dd*, both *J* = *ca.* 8.0, 1H); 9.72 (*t*, *J* = 1.5, 1H). MS: 98 (42), 83 (94), 69 (82), 55 (38), 43 (100).

Scheme 2



2.2. *(1R,3S)-1-(2,2,3-Trimethylcyclobutyl)-1-ethanone ((1R,3S)*-**10***)*. A mixture of 5.80 g of (1*R*,3*R*)-**9** (34.5 mmol) and 36.4 g of tris(triphenylphosphine)chlororhodium (49.9 mmol, partially suspended) and 315 ml of benzene was heated to reflux for 63 h. After cooling to r.t., pentane was added which partially precipitated the Rh(I)-complexes formed and the precipitate was filtered off. Removal of the solvents, a second precipitation, filtration and removal of the solvent, followed by distillation afforded 3.20 g of (1*R*,3*S*)-**10** (66%), b.p. 58–60°/12 Torr, $[\alpha]_D^{20} = -86.8°$ ($c = 1.09$). IR: 1700. ^{1}H-NMR: 0.78, 1.23 (*s*, 3H each); 0.84 (*d*, $J = 6.0$, 3H); 1.50–2.00 (*m*, 3H); 1.93 (*s*, 3H); 2.77 (*dd*, both $J = ca.$ 8.0, 1H). MS: 140 (3, M^+); 83 (100), 71 (23), 70 (93), 55 (88), 43 (49).

2.3. *The Mixture of C(2)-epimeric 2-(2',2',3'-Trimethylcyclobutyl)-3-butyn-2-ols ((1'R,3S)*-**11***)*[8])[9]). A solution of 2.84 g of (1*R*,3*S*)-**10** (20.3 mmol) in 15 ml of THF was added dropwise (*ca.* 25 min) to a cooled (+5°) solution of 2.85 g of lithium acetylide-1,2-diaminoethane complex (31.0 mmol) in 25 ml of THF. The resulting mixture was stirred at r.t. for 26 h and then poured onto ice. The usual workup and distillation afforded 2.44 g of (1'*R*,3'*S*)-**11** (72%), b.p. 76–84°/12 Torr. IR: 3320, 3460. ^{1}H-NMR[8]): 0.86 (br. *d*, $J = 6.0$, 3H); 1.08 (br. *s*, 6H); 1.37 (*s*, 3H); 1.50–2.20 (*m*, 4H); 2.34 (br. *s*, 1H); 2.45 (OH). MS: 109 (100), 70 (85), 69 (21), 55 (61), 43 (31).

2.4. *The Mixture of 6-(2',2',3'-Trimethylcyclobutyl)-4,5-heptadien-2-ones with Different Allene Chiralities ((1'R,3'S)*-**12***)*[8])[9])[10]). A mixture of 2.09 g of (1*R*,3*S*)-**11** (12.6 mmol, *2.3*), 2.74 g of 2-methoxypropene (38.0 mmol), 10 ml of hexane, 10 mg of hydroquinone, and 5 mg of *p*-toluenesulfonic acid hydrate was heated (75°) in a sealed tube for 50 h. The resulting mixture was cooled to r.t., diluted with pentane, and washed with cold (5°) dil. aq. $NaHCO_3$-solution. Drying, removal of the solvents, and distillation gave 1.45 g of (1'*R*,3'*S*)-**12** (56%), b.p. 54–56°/0.01 Torr. IR: 1715, 1960. ^{1}H-NMR: 0.79 (*s*, 3H); 0.81 (*d*, $J = 5.5$, 3H); 1.09 (*s*, 3H); 1.58 (*d*, $J = 3.0$, 3H); 1.30–2.50 (*m*, 4H); 2.09 (*s*, 3H); 3.02 (*d*, $J = 7.0$, 2H); 4.90–5.40 (*m*, 1H).

2.5. *(3E,5Z,1'S,3'S)- and (E,E,1'S,3'S)-6-(2',2',3'-Trimethylcyclobutyl)-3,5-heptadien-2-one ((3E,5Z, 1'S,3'S)*-**5** *and (E,E,1'S,3'S)*-**5***)*. 0.2 ml of 1N methanolic NaOH was added to a cooled (−5°) solution of 1.45 g of (1'*R*,3'*S*)-**12** (*2.4*) in 6 ml of pentane and the mixture then stirred at 5° for 1 h. The resulting mixture

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[8]) The 60-MHz ^{1}H-NMR spectrum appeared as that of a single compound. GC did not separate the diastereoisomers.

[9]) The specific rotation was not measured because this is a mixture of diastereoisomers.

[10]) The MS was not recorded because the compound would have isomerized in the inlet of the spectrometer.

was taken up in pentane and washed with H_2O. Drying, removal of the solvent, and distillation afforded 0.95 g of a *ca.* 3:1 mixture (GC) of (3*E*,5*Z*,1'*S*,3'*S*)-**5**[11] and (*E*,*E*1'*S*,3'*S*)-**5**[11] (together 66%), b.p. 67–68°/0.01 Torr.

*Data for (3*E,5Z,1'S,3'S*)*-**5**. $[\alpha]_D^{20} = +123.4°$ ($c = 1.05$). IR: 1585, 1620, 1665, 1685. ^{1}H-NMR: 0.81 (*s*, 3H); 0.90 (*d*, $J = 6.0$, 3H); 1.13 (*s*, 3H); 1.86 (br. *s*, 3H); 1.50–2.10 (*m*, 3H); 2.13 (*s*, 3H); 2.90–3.35 (*m*, 1H); 5.87 (br. *d*, $J = 15.0$ 1H); 6.02 (br. *d*, $J = 11.0$, 1H); 7.35 (*dd*, $J = 15.0$ and 11.0, 1H). MS: 206 (8, M^+), 136 (60), 121 (100), 93 (68), 83 (43), 55 (44), 43 (62).

*Data for (*E,E,1'S,3'S*)*-**5**. $[\alpha]_D^{20} = -29.9°$ ($c = 1.02$). IR: 1590, 1625, 1665, 1685. ^{1}H-NMR: 0.71 (*s*, 3H); 0.86 (*d*, $J = 6.0$, 3H); 1.17 (*s*, 3H); 1.40–2.80 (*m*, 4H); 1.84 (br. *s*, 3H); 2.17 (*s*, 3H); 5.78 (*d*, $J = 11.0$, 1H); 5.98 (*d*, $J = 15.0$, 1H); 7.32 (*dd*, $J = 11.0$ and 15.0, 1H). MS: 206 (2, M^+), 136 (53), 121 (100), 93 (65), 55 (25), 43 (53).

2.6. *Photochemical Isomerization.* A solution of 0.95 g of the mixture obtained in *2.5* in 45 ml of pentane was irradiated for 2 h with a *Philips HPK* 125-W high-pressure Hg-lamp in a pyrex apparatus fitted with a water-cooled mantle. Removal of the solvent and distillation gave 0.60 g (63%) of a *ca.* 1:10 mixture[11] of (3*E*,5*Z*,1'*S*,3'*S*)-**5** and (*E*,*E*,1'*S*,3'*S*)-**5**.

2.7. *Thermolysis.* Through a dropping funnel fitted with an N_2-inlet and bypass, a solution of 0.60 g of the mixture obtained in *2.6* in *ca.* 20 ml of pentane was dropped at atmospheric pressure into a vertically mounted, electrically heated (*ca.* 310°) quartz tube filled with quartz rings[12]. The products and pentane were collected in a series of cooled (−75°) traps. Evaporation of the pentane afforded 0.52 g of a complex mixture. GC showed 5 major components, among these **1**, **3**, and **6**, and at least 5 minor components. (2*S*, 6*S*)-**3** ($[\alpha]_D^{20} = +306°$ (CCl_4, $c = 0.980$)) was isolated by GC and identified by its spectra [3]. **1** was only identified by GC and the amounts of **1**, **3**, and **6** in the mixture (see below, *3*) were estimated by GC.

Data for 1-(4-Methyl-1,3-cyclohexadienyl)-1-ethanone (**6**). ^{1}H-NMR: 1.85 (br. *s*, 3H); 2.20 (*s*, 3H); 1.90–2.50 (*m*, 4H); 5.82 (br. *d* (weak further splitting), $J = 6.0$, 1H); 6.84 (br. *d*, $J = 6.0$, 1H). MS: 136 (40, M^+), 121 (94), 93 (38), 91 (58), 77 (54), 43 (100).

3. Identification of *trans*-γ-Irone (**7**). – GC/MS coupling of our oil [3] and Professor *Mori*'s sample was carried out on a *Finnigan MAT 4021* system equipped with a 60-m glass capillary column coated with *UCON HB 5100*.

4. Conformations of the α-Irones. – 360-MHz ^{1}H- and 90.55-MHz ^{13}C-FT-NMR spectra of (+)-**1** and (+)-**3** isolated from our oil as described [3] were recorded on a *Bruker WH 360* instrument. Chemical shifts are expressed in ppm (δ-scale) downfield from TMS as an internal standard.

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[11] The assignment of the geometry of the C(3)–C(4) double bond, which is which, is tentative. The thermolysis of the mixture obtained in *2.5* was also carried out and the yields of **1** and **3** were much lower than those obtained with the mixture obtained in *2.6*.

[12] In preliminary experiments, the temperature was adjusted so that a single passage through the tube effected complete conversion of the substrates.

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