

38. On the Stereochemistry of the Irones

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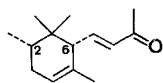
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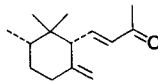
Summary

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].

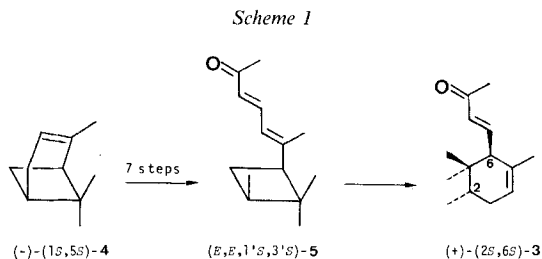
¹⁾ Numbering of the C-atoms according to the *IUPAC* tentative rules for the nomenclature of carotenoids [2], different from that used in [3] [4] and [5].

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 obtained³⁾ samples of irones⁴⁾ that had been distilled in Ruzicka's laboratory in 1950 from which we isolated⁴⁾ (+)-**1** ($[\alpha]_D^{20} = +55^\circ$ (CH_2Cl_2 , $c = 0.879$)) and (+)-**2** ($[\alpha]_D^{20} = +2^\circ$ (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** ($[\alpha]_D^{20} = -43.75^\circ$ (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] ($[\alpha]_D^{20} = +306^\circ$ (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-

³⁾ From D. Felix and A. Eschenmoser.

⁴⁾ 'Fraktionen 17, 18, 21, 22, zweite Destillation an der Podbielniak-Kolonne, 17.3.1950.' (+)-**1** ($[\alpha]_D^{20} = +55^\circ$) was isolated by GC from 'Fraktion 17' which consisted of about 95% of (+)-**1** and 5% of **2** as determined by GC analysis. (+)-**2** ($[\alpha]_D^{20} = +2^\circ$) 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 $\alpha_D = +49^\circ$ 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 $\alpha_D = +13.7^\circ$ and $+5.7^\circ$. The same paper [8] also correctly identifies (+)-*trans*-irone ((+)-**3**) with $\alpha_D = +327^\circ$. 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** → (*2S,6S*)-**3**, a [1,3]-sigmatropic shift, leaves the chiral integrity of the center that becomes C(2) in (*2S,6S*)-**3** largely intact and thus establishes the (*2S*)-configuration of (+)-**3**.

Two further components of the mixture, namely *cis*- α -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 (–)-(*2R,6R*)-**3** starting from (+)-(*R*)-citronellal [4]⁵⁾ which independently establishes the (*2R*)-configuration of (–)-**3**.

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

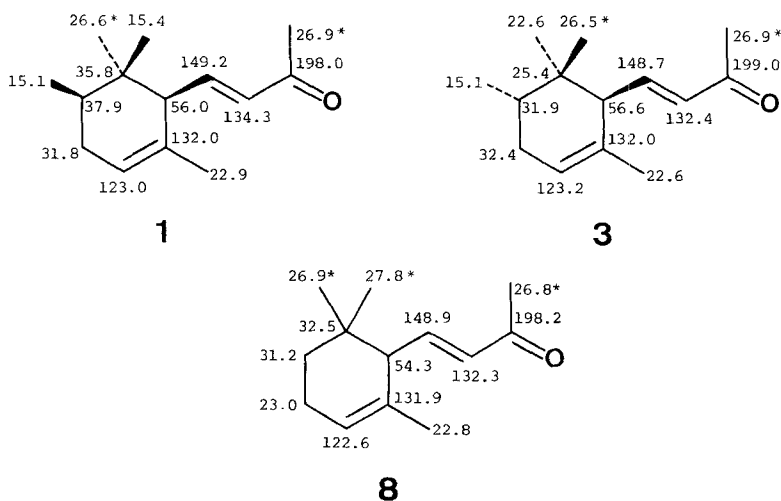
4. The Missing γ -Irone. – We were struck by the fact that our oil [3] contained both the *cis*- α -irone (*2R,6S*)-**1** and the *trans*- α -irone (*2S,6S*)-**3**, but only a single γ -irone, the *cis*- γ -irone (*2R,6S*)-**2**. The missing *trans*- γ -irone (**7**) was also not detected in our isomerization experiments [3] and in *Jaenicke*'s chemical degradation work [1] [6]. Two syntheses of its racemate ((*2RS,6RS*)-**7**) [5] [16] and one of (+)-(*2R,6R*)-**7** (*Yoshikoshi*'s precursor of (*2R,6R*)-**3** [4]) have since been reported. A sample of (*2RS,6RS*)-**7** kindly furnished by Professor *K. Mori* [16] has now enabled us to identify a trace of **7** in our oil by GC/MS coupling⁶⁾.

5. Conformations of the α -Irones. – We had deduced from the CD spectra that the preferred conformations of the *cis*- α -irones (**1**), *trans*- α -irones (**3**), and α -ionones (**8**) in solution are half chairs with the side chain pseudoaxial [3] [18]. By 360-MHz ¹H- and 90.55-MHz ¹³C-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)–CH₃ *d*, the 360-MHz ¹H-NMR spectrum⁷⁾ of **1** in CDCl₃-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)–CH₃ 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 (CDCl₃) virtually the same *dd* was seen. Hence the C(2)–CH₃ must again be equatorial and the side chain now pseudoaxial.

⁵⁾ *Yoshikoshi et al.* erroneously state [4] that we [3] showed that our irones all had the (*2R*)-configuration¹⁾. In fact our irones all had the (*6S*)-configuration¹⁾ [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 CDCl₃-solutions but ¹H-NMR spectra of **1** and **3** in CD₃CN-, C₆D₆- and C₆D₅CD₃-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 CH₃CN-solution and these did not differ significantly from our earlier spectra [3] [18]. Thus we observe the same conformers by CD and NMR.



*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].

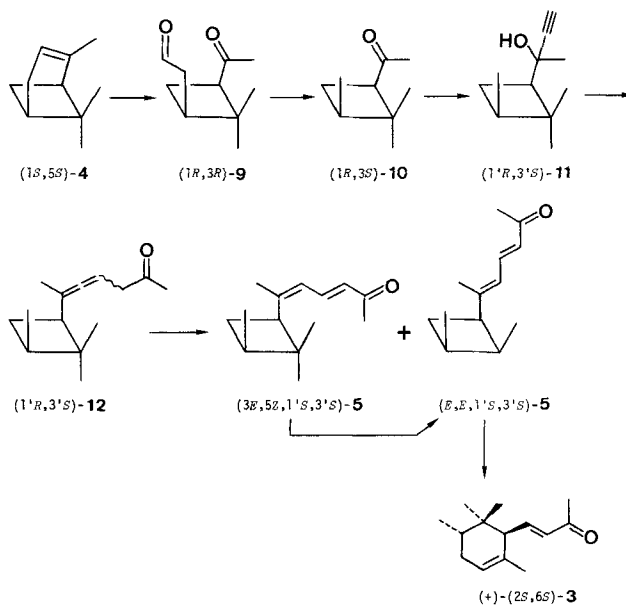
Experimental Part

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 ^1H -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 $\geq 98\%$ 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), $\alpha_D^{20} = -37.43^\circ$ (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. $73\text{--}74^\circ/0.01$ Torr, $[\alpha]_D^{20} = -67.4^\circ$ (*c* = 1.08). IR: 1700, 1720. ^1H -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 (*1R,3R*)-**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 (*1R,3S*)-**10** (66%), b.p. 58–60°/12 Torr, $[\alpha]_D^{20} = -86.8^\circ$ ($c = 1.09$). IR: 1700. $^1\text{H-NMR}$: 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 $J = \text{ca. } 8.0$, 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-buten-2-ols* ((*1'R,3'S*)-**11**)⁸⁾. A solution of 2.84 g of (*1R,3S*)-**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. $^1\text{H-NMR}$ 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⁾. A mixture of 2.09 g of (*1R,3S*)-**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. $^1\text{H-NMR}$: 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

⁸⁾ The 60-MHz $^1\text{H-NMR}$ 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 H₂O. 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*,5*Z*,1'*S*,3'*S*)-**5**. [α]_D²⁰ = +123.4° (*c* = 1.05). IR: 1585, 1620, 1665, 1685. ¹H-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**. [α]_D²⁰ = –29.9° (*c* = 1.02). IR: 1590, 1625, 1665, 1685. ¹H-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 mixture¹¹) 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 N₂-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 rings¹²). 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** ([α]_D²⁰ = +306° (CCl₄, *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**). ¹H-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 ¹H- and 90.55-MHz ¹³C-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.

REFERENCES

- [1] W. Krick, F.-J. Marner & L. Jaenicke, Z. Naturforsch., C 38, 179 (1983).
- [2] O. Isler, 'Carotenoids', Birkhäuser, Basel, 1971.
- [3] V. Rautenstrauch & G. Ohloff, Helv. Chim. Acta 54, 1776 (1971); *idem*, *ibid.* 55, 2686 (1972).
- [4] M. Miyashita, N. Makino, M. Singh & A. Yoshikoshi, J. Chem. Soc., Perkin Trans. 1 1982, 1303.
- [5] J. Garnero & D. Joulain, Bull. Soc. Chim. Fr. 1979, II-15.
- [6] W. Krick, F.-J. Marner & L. Jaenicke, Helv. Chim. Acta 67, 318 (1984).
- [7] E. Gildemeister & F. Hoffmann, 'Die ätherischen Öle', 4. ed., Vol. IV, Akademie-Verlag, Berlin, 1956, p. 460.
- [8] H. H. Günthard, C. F. Seidel & L. Ruzicka, Helv. Chim. Acta 35, 1820 (1952); C. F. Seidel & L. Ruzicka, *ibid.* 35, 1826 (1952).
- [9] L. Ruzicka, C. F. Seidel, H. Schinz & C. Tavel, Helv. Chim. Acta 31, 257 (1948).
- [10] H. E. Eschmazi, J. Am. Chem. Soc. 81, 2905 (1959); *idem*, J. Org. Chem. 26, 3140 (1961).

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.

- [11] *W.S. Johnson, B. Frei & A.S. Gopalan*, J. Org. Chem. **46**, 1512 (1981).
- [12] *K. Ohno & J. Tsuji*, J. Am. Chem. Soc. **90**, 99 (1968).
- [13] *O.F. Beumel Jr. & R.F. Harris*, J. Org. Chem. **29**, 1872 (1964).
- [14] *G. Saucy & R. Marbet*, Helv. Chim. Acta **50**, 1158 (1967).
- [15] *L.M. Jordan*, Ph. D. Thesis, Yale University, 1974. *J.J. Gajewski*, 'Hydrocarbon Thermal Isomerizations', Academic Press, New York, 1981, p.177.
- [16] *T. Kitahara, K. Tanida & K. Mori*, Agric. Biol. Chem. **47**, 581 (1983).
- [17] *W.E. Steinmetz*, J. Am. Chem. Soc. **96**, 685 (1974).
- [18] *G. Ohloff, E. Otto, V. Rautenstrauch & G. Snatzke*, Helv. Chim. Acta **56**, 1874 (1973); *idem*, *ibid.* **59**, 352 (1976).
- [19] *N. Harada*, J. Am. Chem. Soc. **95**, 240 (1973).