156. New Irone-Related Constituents from the Essential Oil of *Iris germanica* L.

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Dedicated to Dr. *G. Ohloff* on the occasion of his 65th birthday

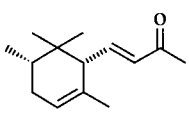
(22.VI.89)

Twenty irone-related compounds **1–20** containing from 10 to 16 C-atoms have been identified for the first time in commercial *Iris* oil of Moroccan origin (*Iris germanica* L.). Most of the structures and the absolute configurations of natural **6**, **16**, and **17** are corroborated by partial synthesis. The organoleptic properties of some of the new constituents are discussed.

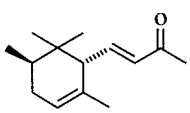
1. Introduction. – *Iris* oil is a fascinating material to investigate for several reasons:

a) It is one of the most valuable natural products used in perfumery (*ca.* 25 000.– SFr./kg for the absolute oil).

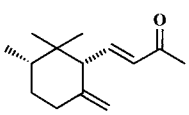
b) The major fragrant constituents are the irones which, for such small molecules, have had an exceptionally long and thorny history. After their first isolation in 1893 [1], it took some 50 years to elucidate their correct constitutions [2] [3], and another 24 years to determine their configurations [4].



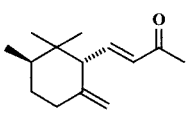
cis-α-irone



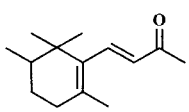
trans-α-irone



cis-γ-irone



trans-γ-irone



β-irone

c) Some years ago, *Jaenicke* and *Marner* [5] were able to shed light on the biosynthesis of these unusual compounds by showing that natural irones are formed by slow air oxidation of C_{31}-triterpenoids produced in *Iris* rhizomes. The same authors found that both enantiomeric forms of irones occur in *Iris* oil of different origin [6].

[1]) New address: *Acima AG*, CH–9470 Buchs/SG.

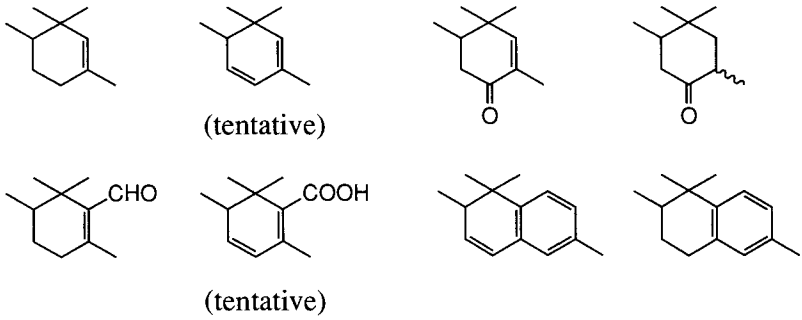


Fig. 1. *Reported irone-type compounds from* Iris *species* [7]

d) Only a few irone-related compounds with the typical additional secondary Me group (*Fig. 1*) have been identified in addition to the well-known α-, β-, and γ-irones[2]) in a recent analysis of *Iris* oil [7]. We felt that further analytical work using GC/MS should reveal additional new irone-type compounds in *Iris* oil with interesting organoleptic properties.

We report the identification of 20 new constituents, compounds **1–20** (*Fig. 2*) from commercial Moroccan *Iris* oil ('Orris butter' or 'Orris concrète'). The compounds are arranged according to their number of C-atoms (from C_{10} to C_{16}). To the best of our knowledge, none of them has been reported to occur in nature.

These compounds were isolated by the usual techniques (chemical separation, column chromatography on silica gel, prep. GC) and identified by spectroscopic methods (*Chapt. 2*).

Our starting material was purchased from Morocco and was obtained from *Iris germanica* L. [8]. This is confirmed by the negative $[\alpha]_D$ value of the irone mixture obtained from this oil and the low content of *trans*-α-irone, two properties typical for *Iris germanica* L. [6][9]. The composition of the irones and the optical rotation of the two major components are given in *Table 1* to characterize our starting material. The values are practically identical with those reported for Moroccan *Iris* oil [6].

Table 1. *Optical Rotations and Composition of Irones from Our Starting Material*

Compound	Composition [%]	$[\alpha]_D^{20}$
cis-α-Irone	61.5	–96.3
trans-α-Irone	0.8	–
β-Irone	1.0	–
cis-γ-Irone	36.7	–5.3

[2]) For a discussion of the occurrence of different irone isomers and enantiomers, see [6].

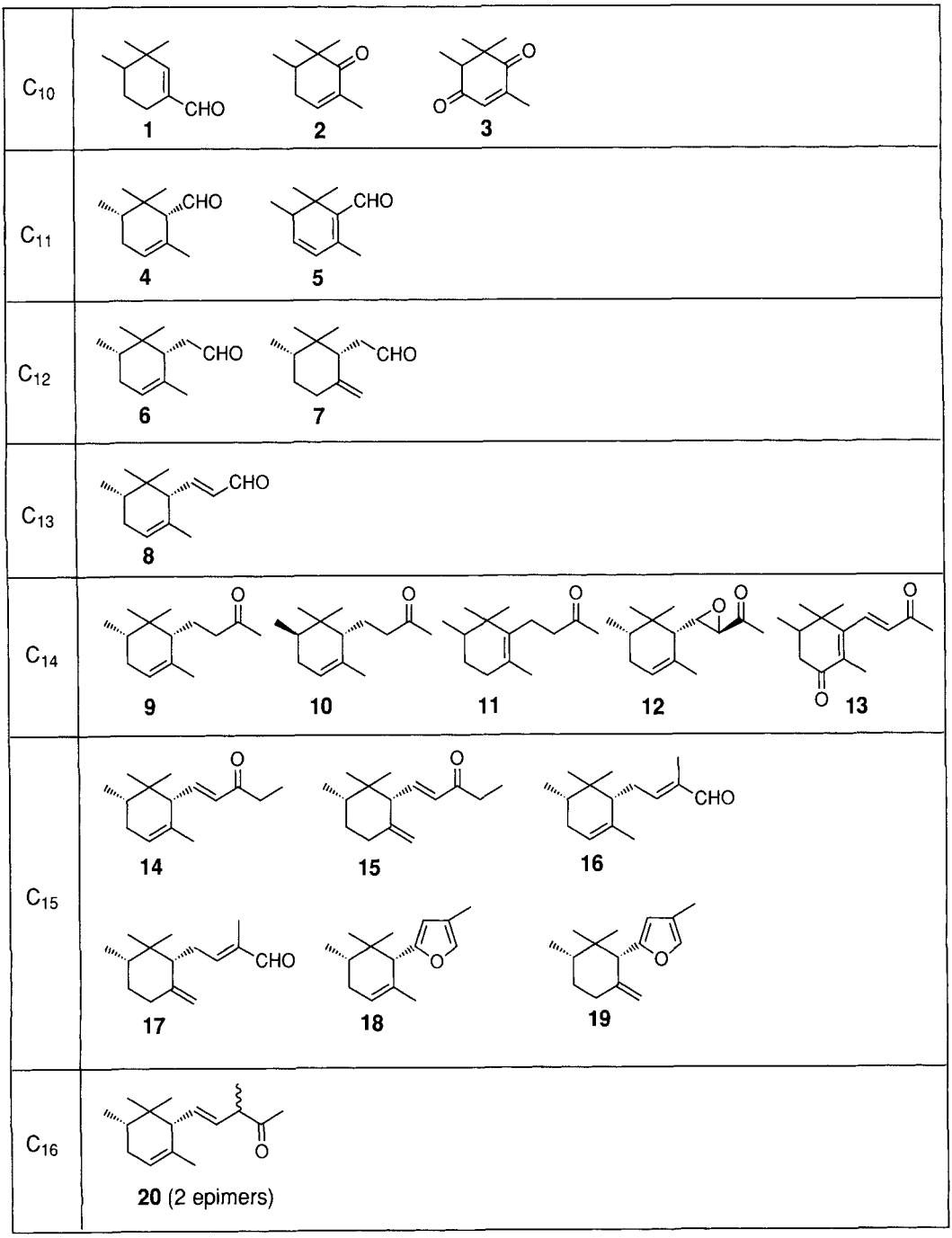
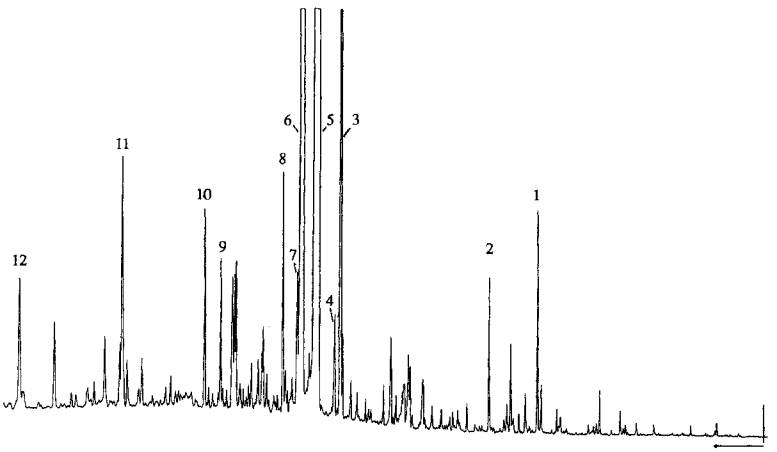


Fig. 2. *New constituents of* Iris *oil*

For a comparison of our work with previous analytical work, a gas chromatogram of the 'absolute oil' obtained from the starting material (see *Exper. Part*) is shown in *Fig. 3*.



1	(*E*)-2-Nonenal	7	β-Irone
2	Ethyl Decanoate	8	Henicosane
3	Dihydro-β-irone	9	Ethyl Palmitate
4	*trans*-α-Irone	10	Tricosane
5	*cis*-α-Irone	11	Pentacosane
6	*cis*-γ-Irone	12	Heptacosane

Fig. 3. *Gas chromatogram of distilled* Iris *absolute (starting material).* Conditions: fused silica capillary column *Supelcowax*™ 60 m, i.d. 0.25 mm, film thickness 0.25 μm; temp. program 80° (5 min) – 250°, 5°/min; carrier gas He.

2. Structure Elucidations and Partial Syntheses. – The structures of the new constituents **1–20** were established by 360-MHz ^{1}H-NMR spectroscopy (making extensive use of selective decoupling techniques) in combination with IR and MS. For the compounds **1**, **6**, **7**, **9**, **10**, and **11**, the spectral data were in agreement with published ones, and for **2–4**, **8**, and **12–18**, the structures derived from the spectra were confirmed by partial synthesis. The structures of the remaining constituents **5**, **19**, and **20** follow unambiguously from their spectral data.

Optical rotations could be measured for *cis*-α-irone, *cis*-γ-irone, **6**, **16**, and **17**. These compounds all belong to the same enantiomeric series (2*S*)[3]), as shown by chemical correlation with optically active *cis*-α-irone and *cis*-γ-irone of known [4] absolute configuration. We therefore assume the newly identified compounds to possess the chiralities shown in *Fig. 2*[4]).

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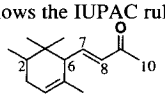
[3]) The numbering of the irones follows the IUPAC rules for the nomenclature of carotenoids.



[4]) *trans*-α-Dihydroirone (**10**) is assumed to possess (2*R*) chirality based on *Rautenstrauch*'s work [4].

^{13}C-NMR data are listed in *Table 2*. The known spectra of the irones are added for comparison. Unfortunately, there are a few compounds (**1**, **5**, **7**, **11**, **13**, **18**, **19**, and **20**) for which we had insufficient material to record ^{13}C-NMR spectra.

3,3,4-Trimethylcyclohex-1-enecarbaldehyde (**1**). The structure of this trace constituent was readily deduced from its ^{1}H-NMR and MS. The NMR spectrum was in agreement with the published data [10]. The compound was reported as a synthetic intermediate in an irone synthesis; its natural occurrence has not been described.

2,5,6,6-Tetramethylcyclohex-2-en-1-one (**2**) *and 2,5,6,6-Tetramethylcyclohex-2-ene-1,4-dione* (**3**). Natural **2** from *Iris* oil was identical with an authentic sample[5]) by its spectral and chromatographic data.

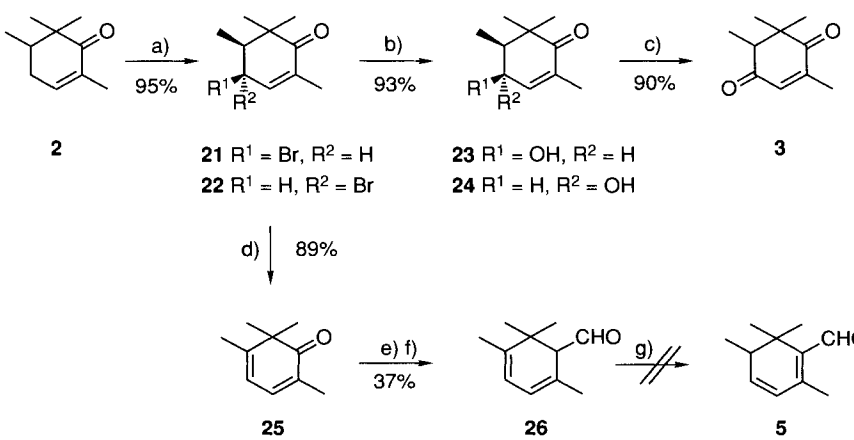
The structure of the closely related diketone **3** was deduced solely from the MS and confirmed by synthesis (*Scheme 1*).

Direct auto-oxidation of **2**, in contrast to isophorone, does not lead to allylic oxidation. Therefore, **2** was subjected to allylic bromination with NBS to give the diastereoisomeric bromo-ketones **21** and **22** (ratio *ca.* 1:1, crude yield *ca.* 95%). The crude product was converted with Ag_2CO_3 in acetone to a mixture of the hydroxy-ketones **23** and **24** (yield 93%) which were oxidized with PCC to give the dione **3** in 90% yield. The t_R and MS of this new compound were identical with natural **3**.

cis-*2,5,6,6-Tetramethylcyclohex-2-enecarbaldehyde* (**4**). Natural **4** was identical (t_R, MS) with a synthetic sample of (±)-**4**, prepared from ketone **2**[6]).

2,5,6,6-Tetramethylcyclohexa-1,3-dienecarbaldehyde (**5**). The mass spectrum ($M^{+\cdot}$ at *m/z* 164) and the ^{1}H-NMR spectrum (16 H-atoms) indicated the empirical formula $C_{11}H_{16}O$.

Scheme 1



2 **21** R^1 = Br, R^2 = H; **22** R^1 = H, R^2 = Br **23** R^1 = OH, R^2 = H; **24** R^1 = H, R^2 = OH **3**

25 **26** **5**

a) NBS, $(PhCOO)_2$, CCl_4/reflux, 2.5 h; b) Ag_2CO_3, acetone/r.t., 3 h; c) PCC, CH_2Cl_2/r.t., 3 h; d) $NaHCO_3$, DMSO/150°, 1 h; e) Me_3SI, NaH, DMSO/r.t., 24 h; f) $MgBr_2$, Et_2O/0°, 1 h; g) Et_3N/100°, 15 h.

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[5]) We thank Dr. *C. Margot, Firmenich SA*, for a generous gift of (±)-**2**, obtained by methylation of commercially available *cis/trans*-2,5,6-trimethylcyclohex-2-en-1-one.

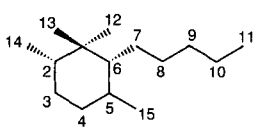
[6]) We thank Dr. *C. Chapuis, Firmenich SA*, for a sample of (±)-**4**.

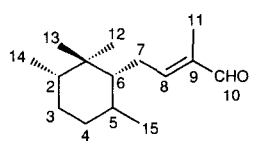
Table 2. *^{13}C-NMR Data for Irone-Type Compounds*

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	C(14)	C(15)
cis-α-Irone[a])	35.8	38.0	31.7	123.1	132.0	56.1	149.2	134.4	197.8	26.9	–	15.1	26.6	15.4	22.7
trans-α-Irone[a])	35.4	32.0	32.4	123.2	132.1	56.6	148.5	132.5	198.2	26.9	–	20.8	26.5	15.1	22.6
cis-γ-Irone[a])	38.8	42.0	32.0	36.3	148.8	57.9	146.9	133.7	197.8	27.2	–	14.4	27.7	15.9	108.8
2[a])	45.2	39.0	31.9	141.8	133.8	204.4	–	–	–	–	–	18.4	22.8	15.6	16.3
3	49.2	53.4	201.1	136.1	147.9	204.1	–	–	–	–	–	21.6	24.5	11.2	16.6
4	35.6	37.6	31.7	125.0	128.4	64.2	205.1	–	–	–	–	16.1	27.1	14.7	22.0
6	35.8	38.5	32.1	123.3	134.1	45.2	43.7	202.8	–	–	–	15.1	26.6	16.0	22.7
8	35.9	37.8	31.7	123.5	131.4	56.2	159.8	136.1	193.5	–	–	15.1[b])	26.6	15.3[b])	22.8
9	36.2	38.7	32.0	122.7	135.4	50.5	22.1	45.7	208.5	29.9	–	15.9	26.4	14.5	22.6
10	35.4	31.8	32.6	121.3	136.1	51.2	24.7	44.3	208.9	29.9	–	23.7	25.7	15.5	21.4
12[a])	36.0	38.1	31.9	125.4	130.6	53.5	58.7	59.9	205.8	24.4	–	15.1[b])	26.9	15.2[b])	22.4
14	36.1	38.3	32.2	123.2	132.5	56.5	147.8	133.5	200.5	33.5	8.4	15.6	26.9	15.6	22.9
15	38.8	42.1	32.0	36.3	149.0	57.9	145.8	132.5	200.7	33.6	8.2	14.4	27.7	15.9	108.7
16[a])	36.1	38.6	31.8	123.7	134.4	50.6	28.3	157.3	138.1	195.0	9.4	14.6	26.6	15.8	22.7
17	39.3	42.3	33.1	37.5	148.5	53.7	25.7	156.5	138.9	195.3	9.4	14.0	26.7	16.4	107.8

[a]) Assignments by ^{13}C,^{1}H-2D-correlation spectroscopy.
[b]) Assignments may be interchanged.

Carotenoid numbering:





The ^{1}H-NMR spectrum revealed the presence of an aldehyde (10.13 (*s*, 1 H)), two Me groups on a quaternary C-atom (1.13 and 1.20 (2 *s*, 6 H)), one secondary Me group (0.96 (*d*, *J* = 7, 3 H)), and one Me group on a tetra-substituted double bond conjugated with the CHO group (2.16 (*s*, 3 H)). A second 1,2-disubstituted double bond was indicated by signals for two vinylic protons (5.84 (*dd*, *J* = 9, 1.5, 1 H); 6.06 (*dd*, *J* = 9, 4.5, 1 H)). These data, which are similar for safranal, fully support structure **5** for this compound. An attempt to synthesize **5** failed (*Scheme 1*), because we were not able to isomerize the deconjugated aldehyde **26** into the conjugated isomer **5**.

*(1*R*,5*S*)-2,5,6,6-Tetramethylcyclohex-2-eneacetaldehyde* (**6**) *and* cis-*2,2,3-Trimethyl-6-methylidenecyclohexaneacetaldehyde* (**7**). The structures of both compounds were deduced from their MS and ^{1}H-NMR spectra (see *Exper. Part*). For **6**, a sufficient sample was isolated to measure the ^{13}C-NMR spectrum (see *Table 2*) and the optical rotation ($[\alpha]_D^{20} = +16$ (*c* = 0.8, $CHCl_3$)). The ^{13}C-NMR spectrum supports the proposed structure for **6**. The published ^{1}H-NMR spectra of **6** [11] and **7** [12] are in excellent agreement with our own spectra. Optical rotations were reported for both enantiomers of **6** [11]: +23.5 (*c* = 2.49, CH_2Cl_2) for the (1*R*,5*S*)-isomer and –21.5 (*c* = 1.36, CH_2Cl_2) for the (1*S*,5*R*)-isomer. This establishes the (1*R*,5*S*)-chirality of natural **6**. Both **6** and **7** have been described as synthetic intermediates [11][12] but not yet as natural products.

10-Nor-cis-α-*irone* (**8**). The ^{1}H-NMR spectrum (see *Exper. Part*) was similar to that of *cis*-α-irone, except that the methylcarbonyl function was replaced by a carbaldehyde group. This was also confirmed by the MS which suggested a lower homologue of α-irone. The structure was confirmed by partial synthesis from *cis*-α-irone (*Scheme 2*).

The haloform reaction of (±)-*cis*-α-irone with NaOBr gave an excellent yield of the known acid **27** [13] which was converted to the chloride **28**. *Rosenmund* reduction of the acid chloride furnished, in 93% yield, the new aldehyde (±)-**8** which was identical (t_R, NMR, MS) with the natural compound.

Dihydroirones **9**, **10**, *and* **11**. These known compounds, identified by comparison with authentic samples, have apparently not yet been found in *Iris* oils, although *cis*-α-dihydroirone (**9**) (and the *cis*-γ-isomer) were isolated from the lipid extracts of the rhizomes of *Iris germanica* after chemical oxidation [14].

7,8-Epoxy-cis-α-*dihydroirone* (**12**). The constitution of **12** was suggested by the MS and ^{1}H-NMR spectrum (see *Exper. Part*), but there was no evidence regarding the configuration of the epoxide ring. The natural compound was identical (t_R, ^{1}H-NMR, MS) with the one obtained by epoxidation of (±)-*cis*-α-irone using alkaline H_2O_2 (*Scheme 2*). This reaction produced a single new epoxide to which, by analogy to the reported highly stereoselective *Weitz-Scheffer* reaction of α-ionone [15], we assign the (6*RS*,7*SR*,8*RS*)-configuration[3]).

4-Oxo-β-irone (**13**). This new natural product was identified (t_R on two different capillary columns, MS) by direct comparison with an authentic sample[7]). The racemic compound has been described as a synthetic intermediate [16][17].

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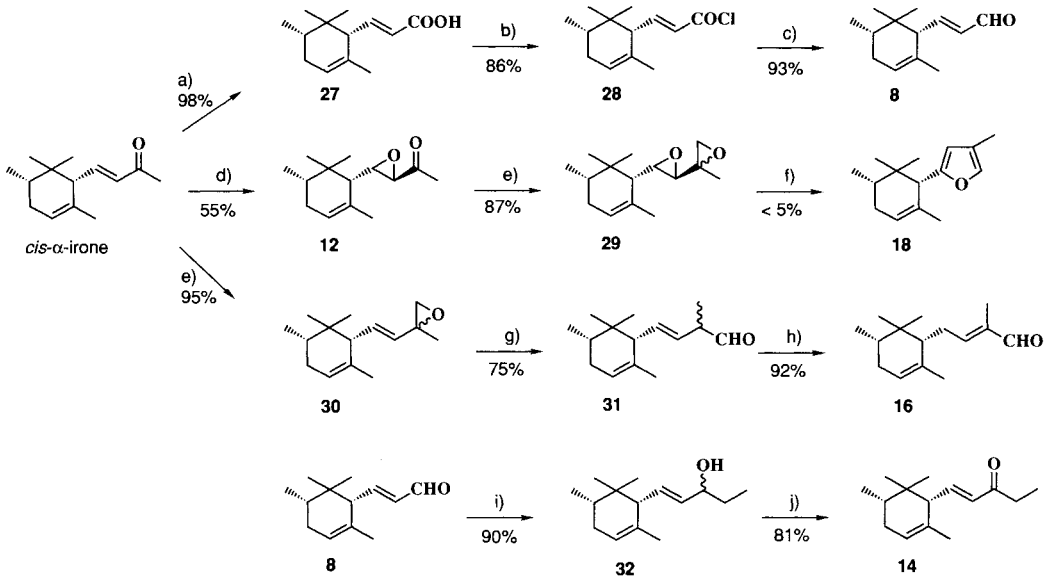
[7]) We thank Dr. *F. Näf* and Mr. *R. Decorzant*, *Firmenich SA*, for a sample of (±)-**13**.

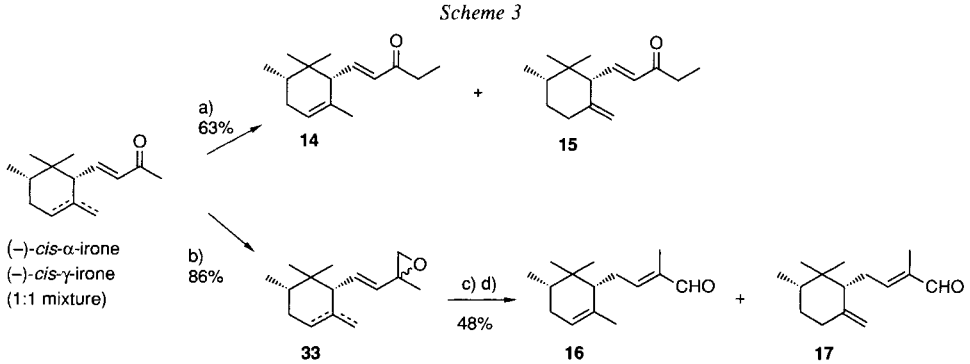
Scheme 2



a) NaOBr, H_2O, dioxane/0° → r.t., 15 h; b) $SOCl_2$/40°, 8 h; c) H_2, Pd/$BaSO_4$ 5%, toluene/reflux, 9 h; d) H_2O_2, NaOH, MeOH/r.t., 72 h; e) Me_3SiI, NaH, DMSO/r.t., 5 h; f) $BF_3 \cdot Et_2O$, Et_2O/r.t., 2 d; g) $MgBr_2$, Et_2O/r.t., 3 h; h) KOH, MeOH/r.t., 2.5 h; i) EtMgBr, Et_2O/reflux, 1 h; j) PCC, CH_2Cl_2/r.t., 3 h.

10-Methyl-cis-*α-irone* (**14**) *and 10-Methyl*-cis-*γ-irone* (**15**). Compound **14** was identical (t_R, ^{1}H-NMR, MS) with an authenic sample prepared from (±)-*cis*-α-irone (*Scheme 2*) *via* aldehyde **8**. Addition of EtMgBr to **8** followed by Cr(VI)-oxidation of the resulting alcohol **32** gave the desired ketone (±)-**14** in good yield and purity (> 98% by GC). Although this method of preparing **14** from *cis*-α-irone is much longer (5 steps) than the direct methylation (*Scheme 3*), it led to pure **14** without the necessity of chromatographic purification steps and is therefore the preferred method for 100-g-scale preparations.

Scheme 3



a) LDA, THF, HMPT, MeI/ –78°, 1 h → r.t., 1 h; b) Me_3SI, NaH, DMSO/r.t., 5 h; c) $MgBr_2$, Et_2O/r.t., 3 h; d) KOH, MeOH/r.t., 2.5 h.

We were not able to isolate sufficiently large and pure samples of **14** and **15** from *Iris* oil to measure their optical rotations. However, both optically active compounds were prepared by methylation of a 1:1 mixture of (–)-*cis*-α-irone ($[\alpha]_D = -96.3$) and (–)-cis-γ-irone ($[\alpha]_D = -5.3$) with MeI (*Scheme 3*). Synthetic **14** and **15** were identical with the natural compounds and showed the following optical rotations: (2*S*,6*R*)-**14**: $[\alpha]_D^{20} = -99.5$ (c = 1.5), (2*S*,6*R*)-**15**: $[\alpha]_D^{20} = +2.5$ (c = 1.5). Compounds **14** and **15** were hitherto not reported.

*(1*R,5S,E*)-2-Methyl-4-(2,5,6,6-tetramethylcyclohex-2-en-1-yl)but-2-enal* (**16**) *and (1*R,3S,E*)-2-Methyl-4-(2,2,3-trimethyl-6-methylidenecyclohex-1-yl)but-2-enal* (**17**). These two new aldehydes were isolated from *Iris* oil in sufficient purity to measure their optical rotations: **16**: $[\alpha]_D^{20} = -9.5$ (c = 1.0), **17**: $[\alpha]_D^{20} = -13.4$ (c = 1.2).

Small samples of both compounds were synthesized in optically active form starting from a 1:1 mixture of (–)-*cis*-α-irone and (–)-*cis*-γ-irone (*Scheme 3*). The synthetic samples of **16** and **17** were identical with the natural compounds and had the following $[\alpha]_D^{20}$ values: **16**: –10.5 (c = 0.5), **17**: –11.0 (c = 1.0). This establishes the absolute configuration of both compounds.

A multi-gram quantity of (±)-**16** was prepared for sensory evaluation from pure (±)-*cis*-α-irone (*Scheme 2*). The *Corey-Chaykovsky* epoxidation [18] of *cis*-α-irone gave in 95% yield an epimeric mixture of epoxides **30**, which, after rearrangement with $MgBr_2$ followed by base-catalyzed isomerization of the deconjugated aldehyde **31**, gave in excellent yield the conjugated racemic aldehyde **16**.

cis-*4-Methyl-2-(2,5,6,6-tetramethylcyclohex-2-en-1-yl)furan* (**18**). The ^{1}H-NMR spectrum (see *Exper. Part*) showed signals for a *cis*-substituted 2,5,6,6-tetramethylcyclohex-2-enyl ring, analogous to those of *cis*-α-irone. In addition, signals at 2.02 (br. *s*, 3 H), 5.92 (*s*, 1 H), and 7.10 ppm (br. *s*, 1 H) indicated the presence of a 2,4-disubstituted furan ring with a Me group at C(4). The absence of characteristic absorption bands in the IR spectrum and the presence of a molecular ion (*m/z* 218) in the MS further supported structure **18** which has the same C-skeleton as **16** and **17**.

The furan of **18** was also obtained by synthesis (*Scheme 2*). The diepoxide **29** (mixture of two diastereoisomers, easily prepared from *cis*-α-irone), upon treatment with acid, gave a complex mixture of products one of which was identical (t_R, ^{1}H-NMR, MS) with the natural compound.

cis-*4-Methyl-2-(2,2,3-trimethyl-6-methylidenecyclohex-1-yl)furan* (**19**). The ^{1}H-NMR-spectrum and MS (see *Exper. Part)* unequivocally identified **19** as the 'γ-isomer' of **18**. Both **18** and **19** are new compounds.

*(*E*)-3-Methyl-5-(*cis*-2,5,6,6-tetramethylcyclohex-2-yl)pent-4-en-2-one* (**20**). The ^{1}H-NMR spectrum of **20** (see *Exper. Part*) clearly establishes the structure and shows the compound to be a 1:1 mixture of C(3)-epimers.

Both, the ^{1}H-NMR and the MS of **20**, show striking similarities to those of the synthetic aldehyde **31** (*Scheme 2*) which may be regarded as a lower homologue of **20**.

3. Discussion. – Whereas *ionones* are widespread in nature and a multitude of structurally related degradation products are known [19], the *irones* so far have been found only in *Iris* oil and, more recently, in oak moss [20]. Irone-related natural compounds with the typical additional Me group are extremely rare outside *Iris* species (*e.g.*, see [21]). Even in *Iris* oil, only a few compounds (see *Fig. 1*) of this type have so far been identified [7] in addition to the well-known irones. Our work has revealed several new irone-related oxidative degradation products among the trace constituents of *Iris* oil. These compounds might have not been noticed during earlier GC/MS analysis [7], because the starting material was probably from a different *Iris* species and had been obtained under different storage conditions of the rhizomes.

The formation of irones and dihydroirones from methylated triterpenoids (cycloiridals) by oxidative degradation is firmly established [5] [6]. It should be no surprise that other oxidation products are also formed during the long storage period (several years) of the peeled rhizomes. While the formation of most of the newly identified compounds from cycloiridals is readily rationalized, the origin of others (*e.g.* **8**, **14**, **15**, and **20**) is not clear.

4. Olfactive Properties of (±)-8, (±)-14, and (±)-16. – It is interesting to compare the odors of the title compounds with that of the highly appreciated, structurally closely related (±)-*cis*-α-irone.

The aldehyde (±)-**8** has the powerful, very pleasant Orris-Violet-like odor of α-irone, but the rooty earthy note, reminiscent of vetiver and typical for *Iris* rhizomes, is more pronounced in (±)-**8**. A very elegant slightly woody note is also discernible. The odor strength of both compounds is about the same.

The odor of the higher irone-homologue (±)-**14** resembles that of (±)-*cis*-α-irone but exhibits fruity undertones and lacks the radiating power of the latter.

Of the three title compounds, the aldehyde (±)-**16** is the least typical. The *Iris* notes are almost absent, and the odor is in the direction of methylionone and much weaker than that of (±)-*cis*-α-irone.

Experimental Part

General. All reactions were carried out under Ar. Column chromatography (CC): silica gel *Merck* (particle size 0.063–0.2 mm). Prep. GC: *Varian Aerograph* series *1800* instrument using *Carbowax 20M*, 2% on *Chromosorb G*, 60–80 mesh (4 mm × 4 m) and silicone *OV-101*, 4% on *Chromosorb G*, 60–80 mesh (4 mm × 4 m). Anal. GC: *Carlo Erba Fractovap* series *2150* using a fused silica capillary column (*Supelcowax*™ 60 m); carrier gas He. Rel. retention times (t_R) of identified natural products (t_R of *cis*-α-irone 1.000) refer to GC using a fused silica capillary column (*Supelcowax*™ 60 m, i.d. 0.25 mm, film thickness 0.25 μm); temp. program 80° (5 min) –250°, 5°/min. $[\alpha]_D$: *Perkin-Elmer-141* polarimeter; in $CHCl_3$ soln. IR spectra: *Perkin-Elmer* 720 spectrometer. ^{1}H- (360 MHz) and ^{13}C-NMR spectra (90.5 MHz): *Bruker WH 360* instrument; in $CDCl_3$ with TMS (= 0.00 ppm) as internal standard; *J* in Hz. MS: *Finnigan MAT* quadrupole instrument coupled with a GC; electron energy *ca.* 70 eV; intensity of M^+ and of the 12 most intense fragment ions in % of the most abundant peak.

1. *Isolation from* Iris *oil.* Commercial *Iris* Concrète of Moroccan origin (probably *Iris germanica*, 300 g) was dissolved in 1.5 l of Et_2O at r.t. To this soln. was added within 10 min a hot soln. of LiOAc · 2 H_2O (300 g) in 1 l of EtOH. After stirring for 2 h at r.t., the precipitate of Li-myristate (*cf.* [22]) was removed by filtration through a glass frit. The filter cake was extracted with Et_2O, and the combined filtrates were washed with 20% aq. Na_2CO_3 soln. to remove excess AcOH. The Et_2O soln. was evaporated to give 81 g of an 'absolute'. Bulb-to-

bulb distillation in 2 equal portions (50–170°/0.1 Torr) gave 52.6 g (17.5%) of distilled *Iris* absolute (GC: see *Fig. 3*).

Repeated CC of the *Iris* absolute on silica gel using cyclohexane/Et_2O 95:5 → 50:50 allowed individual constituents to be enriched. The following compounds were isolated by combined prep. GC on *Carbowax* and *OV 101* columns (in the order of elution on SiO_2).

1,2-Dihydro-1,1,2,6-tetramethylnaphthalene (= *Didehydroirene*). t_R 0.867. ^{1}H-NMR: 0.94 (*d*, *J* = 7, 3 H); 1.21 (*s*, 3 H); 1.24 (*s*, 3 H); 2.22 (*m*, 1 H); 2.30 (*s*, 3 H); 5.85 (*dd*, *J* = 9, 4.5, 1 H); 6.33 (*d*, *J* = 9, 1 H); 6.85 (br. *s*, 1 H); 7.00 (br. *d*, *J* = 8, 1 H); 7.18 (*d*, *J* = 8, 1 H). MS: 186 (28, M^+), 171 (100), 156 (52), 141 (18), 172 (14), 157 (14), 128 (12), 77 (12), 155 (11), 115 (9), 143 (8), 142 (8), 84 (8). Known constituent [7].

1,2,3,4-Tetrahydro-1,1,2,6-tetramethylnaphthalene (= *Irene*). t_R 0.861. ^{1}H-NMR: 0.98 (*d*, *J* = 6, 3 H); 1.12 (*s*, 3 H); 1.29 (*s*, 3 H); 1.53–1.79 (*m*, 3H); 2.27 (*s*, 3H); 2.74–2.78 (*m*, 2H); 6.86 (br. *s*, 1 H); 6.97 (br. *d*, *J* = 8, 1 H); 7.25 (*d*, *J* = 8, 1 H). MS: 188 (25, M^+), 173 (100), 131 (55), 174 (19), 146 (12), 128 (11), 155 (10), 129 (9), 91 (9) 145 (8), 141 (6), 132 (6), 77 (6). Known constituent [7].

cis-*4-Methyl-2-(2,5,6,6-tetramethylcyclohex-2-en-1-yl)furan* (**18**). t_R 0.830. Identical (t_R, ^{1}H-NMR, MS) with the synthetic sample (*Scheme 2*).

cis-*4-Methyl-2-(2,2,3-trimethyl-6-methylidenecyclohex-1-yl)furan* (**19**). t_R 0.876. ^{1}H-NMR: 0.78 (*s*, 3 H); 0.85 (*s*, 3 H); 0.88 (*d*, *J* = 7, 3 H); 1.30–1.43 (*m*, 1 H); 1.47–1.60 (*m*, 2 H); 2.02 (br. *s*, 3 H); 2.11–2.22 (*m*, 1 H); 2.35–2.42 (*m*, 1 H); 3.17 (br. *s*, 1 H); 4.50 (br. *s*, 1 H); 4.78 (br. *s*, 1 H); 5.96 (*s*, 1 H); 7.11 (br. *s*, 1 H). MS: 218 (79, M^+), 135 (100), 91 (54), 41 (45), 108 (44), 95 (36), 121 (35), 55 (35), 107 (33), 83 (30), 105 (27), 134 (26), 123 (25).

(E)-*1-(*cis-*2,5,6,6-Tetramethylcyclohex-2-en-1-yl)pent-1-en-3-one* (= *10-Methyl*-cis-α-*irone*, **14**). t_R 1.048. Identical (t_R, ^{1}H-NMR, MS) with the synthetic compound prepared according to *Scheme 3*.

(E)-*1-(*cis-*2,2,3-Trimethyl-6-methylidenecyclohex-1-yl)pent-1-en-3-one* (= *10-Methyl*-cis-γ-*irone*, **15**). t_R 1.067. Identical (t_R, ^{1}H-NMR, MS) with the synthetic compound prepared according to *Scheme 3*.

*(1*R,5S*)-2,5,6,6-Tetramethylcyclohex-2-eneacetaldehyde* (**6**). t_R 0.855 $[\alpha]_D^{20}$ = +16.0 (*c* = 0.8). ([11]: $[\alpha]_D^{23}$ = +23.5 (*c* = 2.49, CH_2Cl_2)). IR (liq.): 2830, 2720, 1725. ^{1}H-NMR: 0.63 (*s*, 3 H); 0.87 (*d*, *J* = 6, 3 H); 0.92 (*s*, 3 H); 1.49–1.59 (*m*, 1 H); 1.54 (br. *s*, 3 H); 1.64–1.75 (*m*, 1 H); 1.86–1.95 (*m*, 1 H); 2.39–2.56 (*m*, 3 H); 5.43 (br. *s*, 1 H); 9.87 (*m*, 1 H). ^{13}C-NMR: *Table 2*. MS: 180 (1, M^+), 81 (100), 70 (98), 136 (68), 121 (45), 55 (41), 82 (36), 110 (33), 67 (19), 95 (17), 39 (15), 79 (14), 53 (13). The ^{1}H-NMR spectrum is in good agreement with that published in [11].

*(1*R,5S,E*)-2-Methyl-4-(2,5,6,6-tetramethylcyclohex-2-en-1-yl)but-2-enal* (**16**). t_R 1.142. $[\alpha]_D^{20}$ = –9.5 (*c* = 1.0). Identical (t_R, $[\alpha]_D$, ^{1}H-NMR, MS) with an authentic sample (*Scheme 3*).

*(1*R,3S,E*)-2-Methyl-4-(2,2,3-trimethyl-6-methylidenecyclohex-1-yl)but-2-enal* (**17**). t_R 1.133 $[\alpha]_D^{20}$ = –13.4 (*c* = 1.2). Identical (t_R, $[\alpha]_D$, ^{1}H-NMR, MS) with an authentic sample (*Scheme 3*).

2,5,6,6-Tetramethylcyclohex-2-en-1-one (**2**). t_R 0.609. Identical (t_R, MS) with authentic material. ^{1}H-NMR: 0.95 (*s*, 3 H); 0.97 (*d*, *J* = 7, 3 H); 1.13 (*s*, 3 H); 1.76 (*d*, *J* = 1, 3 H); 1.92–2.01 (*m*, 1 H); 2.04–2.15 (*m*, 1 H); 2.27–2.37 (*m*, 1 H); 6.59 (*m*, 1 H). ^{13}C-NMR: *Table 2*. MS: 152 (8, M^+), 82 (100), 54 (18), 41 (7), 39 (7), 83 (6), 55 (6), 53 (5), 67 (4), 109 (3), 79 (2), 77 (2), 124 (1).

cis-*2,5,6,6-Tetramethylcyclohex-2-enecarbaldehyde* (**4**). t_R 0.685. Identical (t_R, MS) with an authentic sample[6]. IR (liq.): 2840, 2720, 1725. ^{1}H-NMR: 0.87 (*d*, *J* = 7, 3 H); 0.91 (*s*, 3 H); 0.99 (*s*, 3 H); 1.40–1.50 (*m*, 1 H); 1.63 (br. *s*, 3 H); 1.76–1.87 (*m*, 1 H); 1.98–2.08 (*m*, 1 H); 2.54–2.59 (*m*, 1 H); 5.64–5.68 (br. *s*, 1 H); 9.65 (*d*, *J* = 5, 1 H). ^{13}C-NMR: *Table 2*. MS: 166 (22, M^+), 95 (100), 41 (87), 137 (69), 108 (60), 81 (56), 39 (54), 55 (52), 70 (42), 57 (41), 67 (38), 135 (37), 43 (36).

cis-*2,2,3-Trimethyl-6-methylidenecyclohexaneacetaldehyde* (**7**). t_R 0.867. ^{1}H-NMR: 0.57 (*s*, 3 H); 0.87 (*d*, *J* = 6, 3 H); 0.98 (*s*, 3 H); 1.27 (*qd*, *J* = 12.5, 4, 1 H); 1.48–1.62 (*m*, 2 H); 2.11 (*td*, *J* = 12.5, 4.5, 1 H); 2.32 (*m*, 1 H); 2.40–2.47 (*m*, 1 H); 2.48–2.63 (*m*, 2 H); 4.41 (*s*, 1 H); 4.84 (*s*, 1 H); 9.65 (*m*, 1 H). MS: 180 (2, M^+), 83 (100), 41 (98), 55 (88), 39 (52), 95 (33), 81 (32), 165 (29), 136 (29), 67 (29), 43 (29), 121 (28), 123 (23). The spectra are in good agreement with published data [12].

(E)-*3-(*cis-*2,5,6,6-Tetramethylcyclohex-2-en-1-yl)prop-2-enal* (= *10-Nor*-cis-α–*irone*, **8**). t_R 0.976. Identical (t_R, ^{1}H-NMR, MS) with an authentic sample (*Scheme 2*).

10-Epijunenol. t_R 0.994. Our spectra (^{1}H-NMR, MS) were identical with published data [23]. The occurrence of this sesquiterpene alcohol in *Iris* species has not been reported.

(E)-*3-Methyl-5-(*cis-*2,5,6,6-tetramethylcyclohex-2-en-1-yl)pent-4-en-2-one* (**20**, 1:1 mixture of C(3)-epimers). t_R 1.033. ^{1}H-NMR: 0.64, 0.65 (2 *s*, 3 H); 0.84 (*s*, 3 H); 0.85 (*d*, *J* = 6, 3 H); 1.18, 1.19 (2 *d*, *J* = 6, 3 H); 1.40–1.50 (*m*, 1 H); 1.53 (br. *s*, 3 H); 1.66–1.77 (*m*, 1 H); 1.85–1.95 (*m*, 1 H); 2.17, 2.18 (2 *s*, 3 H); 2.36 (*m*, 1 H); 3.22 (*m*, 1 H); 5.40–5.47 (*m*, 3 H). MS: 234 (1, M^+), 121 (100), 164 (37), 93 (37), 43 (31), 122 (12), 55 (12), 91 (11), 41 (11), 79 (9), 106 (8), 105 (8), 77 (7).

3,3,4-Trimethylcyclohex-1-enecarbaldehyde (**1**). t_R 0.691. ^{1}H-NMR: 0.93 (*d*, *J* = 7, 3 H); 0.94 (*s*, 3 H); 1.12 (*s*, 3 H); 1.28–1.42 (*m*, 1 H); 1.48–1.68 (*m*, 2 H); 1.99–2.09 (*m*, 1 H); 2.28–2.36 (*m*, 1 H); 6.44 (br. *s*, 1 H); 9.42 (*s*, 1 H); *cf.* [10]. MS: 152 (30, $M^{+\cdot}$), 95 (100), 123 (99), 81 (89), 41 (79), 67 (70), 39 (54), 109 (51), 137 (48), 79 (42), 69 (41), 55 (38), 91 (36).

2,5,6,6-Tetramethylcyclohexa-1,3-dienecarbaldehyde (**5**). t_R 0.800. ^{1}H-NMR: 0.96 (*d*, *J* = 7, 3 H); 1.13 (*s*, 3 H); 1.20 (*s*, 3 H); 2.11 (*m*, 1 H); 2.16 (*s*, 3 H); 5.84 (*dd*, *J* = 9, 1.5, 1 H); 6.06 (*dd*, *J* = 9, 4.5, 1 H); 10.13 (*s*, 1 H). MS: 164 (67, $M^{+\cdot}$), 121 (100), 105 (73), 149 (60), 39 (49), 135 (46), 91 (41), 79 (35), 77 (34), 41 (34), 119 (28), 93 (20), 106 (19).

2,5,6,6-Tetramethylcyclohex-1-enecarbaldehyde. t_R 0.812. Known constituent of *Iris* oil [7]. ^{1}H-NMR: 0.91 (*d*, *J* = 6, 3 H); 1.07 (*s*, 3 H); 1.22 (*s*, 3 H); 1.35–1.50 (*m*, 2 H); 1.53–1.60 (*m*, 1 H); 2.09 (*s*, 3 H); 2.18–2.25 (*m*, 2 H); 10.13 (*s*, 1 H). MS: 166 (70, $M^{+\cdot}$), 81 (100), 41 (91), 109 (77), 39 (73), 151 (62), 123 (57), 95 (51), 43 (46), 133 (41), 137 (40), 148 (35), 55 (35).

*4-(*trans*-2,5,6,6-Tetramethylcyclohex-2-en-1-yl)butan-2-one* (= trans-α-*Dihydroirone*, **10**). t_R 0.948. Identical (t_R, MS) with authentic sample. ^{1}H-NMR: 0.74 (*s*, 3 H); 0.81 (*d*, *J* = 7, 3 H); 0.91 (*s*, 3 H); 1.45 (*m*, 1 H); 1.53–1.64 (*m*, 3 H); 1.66 (br. *s*, 3 H); 1.76–1.86 (*m*, 1 H); 1.92–2.02 (*m*, 1 H); 2.13 (*s*, 3 H); 2.46–2.52 (*m*, 2 H); 5.28 (br. *s*, 1 H). ^{13}C-NMR: *Table 2*. MS: 208 (8, M^{+}), 43 (100), 95 (95), 135 (73), 150 (59), 41 (40), 107 (37), 55 (30), 79 (27), 121 (24), 67 (23), 91 (22), 81 (21).

cis-α-*Dihydroirone* (**9**). t_R 1.009. Identical (t_R, MS) with authentic sample. ^{1}H-NMR: 0.65 (*s*, 3 H); 0.84 (*d*, *J* = 6, 3 H); 0.92 (*s*, 3 H); 1.40–1.56 (*m*, 2 H); 1.60–1.72 (*m*, 2 H); 1.66 (br. *s*, 3 H); 1.80–1.93 (*m*, 2 H); 2.14 (*s*, 3 H); 2.44 (*m*, 1 H); 2.65 (*m*, 1 H); 5.35 (*m*, 1 H). ^{13}C-NMR: *Table 2*. MS: 208 (4, M^{+}), 135 (100), 95 (92), 43 (88), 150 (76), 107 (41), 121 (32), 41 (32), 79 (27), 55 (27), 93 (22), 91 (21), 67 (21). *cf.* [14].

*(*E*)-1-(2,6,6-Trimethylcyclohexa-1,3-dien-1-yl)but-2-en-1-one* (= *Damascenone*). t_R 0.879. Identical (t_R, ^{1}H-NMR, MS) with authentic sample. A new constituent of *Iris* oil.

4-(2,5,6,6-Tetramethylcyclohex-1-en-1-yl)butan-2-one (= β-*Dihydroirone*, **11**). t_R 0.964. Identical (t_R, MS) with an authentic sample. ^{1}H-NMR (60 MHz): 0.83 (*s*, 3 H); 0.90 (*d*, *J* = 5, 3 H); 1.00 (*s*, 3 H); 1.30–2.03 (*m*, 5 H); 1.57 (*s*, 3 H); 2.13 (*s*, 3 H); 2.20–2.50 (*m*, 4 H). MS: 208 (1, M^{+}), 43 (100), 107 (48), 83 (44), 55 (37), 135 (30), 150 (29), 41 (29), 95 (25), 123 (21) 93 (21), 79 (19), 175 (15).

*2,4,4,5-Tetramethyl-3-[(*E*)-3-oxobut-1-enyl]cyclohex-2-en-1-one* (= *4-Oxo-β-irone*, **13**). t_R 1.197. ^{1}H-NMR: 1.01 (*d*, *J* = 6, 3 H); 1.08 (*s*, 3 H); 1.17 (*s*, 3 H); 1.79 (*s*, 3 H); 2.01–2.11 (*m*, 1 H); 2.33 (*dd*, *J* = 17, 11, 1 H); 2.36 (*s*, 3 H); 2.50 (*dd*, *J* = 17, 4.5, 1 H); 6.16 (*d*, *J* = 16, 1 H); 7.27 (*d*, *J* = 16, 1 H); *cf.* [16]. MS: 220 (29, M^{+}), 43 (100), 177 (59), 136 (50), 135 (48), 121 (36), 41 (29), 122 (20), 107 (20), 91 (19), 69 (16), 39 (15), 150 (13); in agreement with [16]. Identical (t_R, MS) with a synthetic sample[7]).

*(1'*R*,3*R*,4*S*,5'*S*)-3,4-Epoxy-4-(2',5',6',6'-tetramethylcyclohex-2'-en-1'-yl)butan-2-one* (= *(2*S*,6*R*,7*S*,8*R*)-7,8-Epoxy*-cis-α-*dihydroirone*, **12**). t_R 1.100. Identical (t_R, ^{1}H-NMR, MS) with an authentic sample (*Scheme 2*).

A stereoisomer of **12** with unknown configuration of the epoxide ring was also isolated from *Iris* oil. t_R 1.092. ^{1}H-NMR: 0.76 (s, 3 H); 0.85 (*d*, *J* = 7, 3 H); 1.03 (*s*, 3 H); 1.41–1.55 (*m*, 2 H); 1.65–1.78 (*m*, 1 H); 1.84 (br. *s*, 3 H); 1.88–2.01 (*m*, 1 H); 2.10 (*s*, 3 H); 2.93 (*dd*, *J* = 9, 2, 1 H); 3.32 (*d*, *J* = 2, 1 H); 5.52 (*m*, 1 H). MS: 222 (< 1, M^{+}), 43 (100), 41 (49), 149 (40), 109 (31), 70 (30), 55 (27), 121 (26), 95 (25), 81 (24), 79 (22), 39 (22), 85 (19).

*(1'*R*,5'*S*,3*E*)-4-(2',5',6',6'-Tetramethylcyclohex-2'-en-1'-yl)but-3-en-2-one* (= *(2*S*,6*R*)-cis-α-*Irone*). t_R 1.000. $[\alpha]_D^{20}$ = –96.3 (*c* = 1.08) ([6]: $[\alpha]_D^{20}$ = –111 (*c* = 8.8)). IR, ^{1}H-NMR, and MS: in agreement with published data [4][13]. ^{13}C-NMR: *Table 2*.

trans-α-*Irone*. t_R 0.976. Identical (t_R, ^{1}H-NMR, MS) with authentic material. IR, MS: in agreement with [4]. ^{1}H-NMR: 0.82 (*s*, 3 H); 0.84 (*d*, *J* = 6, 3 H); 0.85 (*s*, 3 H); 1.56 (br. *s*, 3 H); 1.60–1.74 (*m*, 2 H); 1.99–2.10 (*m*, 1 H); 2.26 (*s*, 3 H); 2.27 (br. *d*, *J* = 9, 1 H); 5.47 (*m*, 1 H); 6.04 (*d*, *J* = 16, 1 H); 6.69 (*dd*, *J* = 16, 9, 1 H). ^{13}C-NMR: *Table 2*.

*(1'*R*,3'*S*,3*E*)-4-(2',2',3'-Trimethyl-6'-methylidenecyclohex-1'-yl)but-3-en-2-one* (= *(2*S*,6*R*)-cis-γ-*Irone*). t_R 1.024. $[\alpha]_D^{20}$ = –5.3 (*c* = 0.75); ([6]: $[\alpha]_D^{20}$ = –1 (*c* = 0.5)). ^{1}H-NMR, ^{13}C-NMR, and MS: in agreement with published data [12][24].

2,5,6,6-Tetramethylcyclohex-2-ene-1,4-dione (**3**). t_R 0.821. Identical (t_R, MS) with an authentic sample (*Scheme 1*).

2. *Synthesis Depicted in* Scheme 1. 2.1. *(±)-2,5,6,6-Tetramethylcyclohex-2-ene-1,4-dione* (**3**). 2.1.1. cis- *and* trans-*4-Bromo-2,5,6,6-tetramethylcyclohex-2-en-1-one* (**21** and **22**, resp.). Ketone (±)-**2**[5]) (15.2 g, 0.10 mol), NBS (21.4 g, 0.12 mol), benzoylperoxide (0.3 g), and dry CCl_4 (150 ml) were heated at reflux for 2 1/2 h and cooled to r.t. The succinimide was removed by filtration and the filtrate evaporated. The crude mixture (22 g, 95%) **21/22** (*ca.* 1:1) was directly used for the next step. Anal. samples of **21** (*Peak 2*) and **22** (*Peak 1*) were isolated by prep. GC (*Carbowax*, 180°).

Data of **21**: ^{1}H-NMR: 1.16, 1.17 (2 *s*, 6 H); 1.21 (*d*, *J* = 7, 3 H); 1.84 (br. *s*, 3 H); 2.14 (*m*, 1 H); 5.00–5.04 (*m*, 1 H); 6.71 (br. *d*, *J* = 3.5, 1 H). MS: 230/232 (2, M^+), 151 (100), 160/162 (31), 123 (31), 41 (31), 39 (30), 81 (29), 43 (22), 53 (21), 109 (14), 91 (14), 79 (13), 55 (12).

Data of **22**: ^{1}H-NMR: 0.96, 1.18 (2 *s*, 6 H); 1.23 (*d*, *J* = 7, 3 H); 1.83 (br. *s*, 3 H); 2.28 (*dq*, *J* = 10,7, 1 H); 4.61–4.68 (*m*, 1 H); 6.75 (br. *s*, 1 H). MS: similar to that of **21**.

2.1.2. cis- *and* trans-*4-Hydroxy-2,5,6,6-tetramethylcyclohex-2-en-1-one* (**23** and **24**, resp.). The crude mixture **21/22** (2:1; 5 g, 21.6 mmol) and Ag_2CO_3 ([25], freshly prepared, 6.10 g (22.1 mmol)) in acetone (60 ml) was stirred at r.t. for 3 h. The Ag salts were filtered and the filtrate evaporated. The residue was taken up in Et_2O and washed with aq. NaCl soln. Evaporation of the solvent gave a mixture (3.4 g, 93.7%) **23/24** (*ca.* 2:1) which was used without further purification for the oxidation. Anal. samples of **23** (*Peak 2*) and **24** (*Peak 1*) were obtained by prep. GC (*Carbowax*, 200°).

Data of **23**: ^{1}H-NMR: 0.94 (*d*, *J* = 7, 3 H); 1.13, 1.18 (2 *s*, 6 H); 1.79 (br. *s*, 3 H); 2.08–2.15 (*m*, 1 H); 4.75 (*m*, 1 H); 6.43 (*m*, 1 H). ^{13}C-NMR: 9.2 (*q*); 16.0 (*q*); 23.1 (*q*); 24.8 (*q*); 46.2 (*s*); 46.4 (*d*); 67.6 (*d*); 133.9 (*s*); 142.9 (*d*); 204.4 (*s*). MS: 168 (6, M^+), 98 (100), 70 (39), 69 (22), 41 (14), 125 (9), 99 (9), 55 (9), 39 (9), 42 (8), 43 (7), 83 (5), 97 (4).

Data of **24**: ^{1}H-NMR: 0.96, 1.13 (2 *s*, 6 H); 1.14 (*d*, *J* = 7, 3 H); 1.79 (br. *s*, 3 H); 1.76–1.85 (*m*, 1 H); 4.09 (br. *d*, *J* = 9, 1 H); 6.59 (*m*, 1 H). ^{13}C-NMR: 11.3 (*q*); 16.2 (*q*); 18.8 (*q*); 22.5 (*q*); 45.7 (*s*); 47.5 (*d*); 70.5 (*d*); 133.5 (*s*); 145.8 (*d*); 204.6 (*s*). MS: similar to that of **23**.

2.1.3. *Oxidation of* **23/24**. The crude mixture **23/24** (3.4 g, 20 mmol) was dissolved in CH_2Cl_2 (60 ml) and stirred in the presence of pyridinium chlorochromate (4.3 g, 20 mmol) and *Celite* (8 g) at r.t. for 3 h. After the addition of cyclohexane (60 ml), the mixture was filtered through *Celite* and the filtrate evaporated. The crude product (3.4 g) was chromatographed on silica gel (600 g) with cyclohexane/Et_2O 95:5→ 50:50 to give 3.0 g (90%) of pure (±)-(**3**) which was identical with the natural compound. Oil. IR (liq.): 1680, 1630. ^{1}H-NMR: 1.09 (*s*, 3 H); 1.17 (*d*, *J* = 7, 3 H); 1.27 (*s*, 3 H); 2.01 (*d*, *J* = 1, 3 H); 2.73 (*q*, *J* = 7, 1 H); 6.54 (br. *s*, 1 H). ^{13}C-NMR: *Table 2*. MS: 166 (27, M^+), 96 (100), 68 (94), 39 (49), 40 (46), 41 (28), 151 (17), 55 (17), 123 (9), 95 (9), 69 (8), 67 (7), 53 (7).

2.2. *Attempted Synthesis of (±)-2,5,6,6-Tetramethylcyclohexa-1,3-dienecarbaldehyde* (**5**). 2.2.1. *2,5,6,6-Tetramethylcyclohexa-2,4-dien-1-one* (**25**). The crude mixture of **21/22** (see *2.1.1*; 4.5 g, 19.5 mmol), $NaHCO_3$ (10 g), and DMSO (50 ml) was stirred at 150° until no more CO_2 was produced (1 h). The mixture was cooled to r.t., poured into ice/water, and extracted with Et_2O. The combined Et_2O extracts were washed with H_2O, dried ($MgSO_4$), and evaporated. Bulb-to-bulb distillation (80°/2 Torr) gave 2.6 g (89%) of **25** (purity by GC >97%) as an oil. ^{1}H-NMR: 1.22 (*s*, 6 H); 1.86 (br. *s*, 3 H); 1.91 (br. *s*, 3 H); 5.91 (br. *d*, *J* = 7, 1 H); 6.78 (br. *d*, *J* = 7, 1 H). ^{13}C-NMR: 15.5 (*q*); 19.3 (*q*); 24.9 (2 *q*); 49.9 (*s*); 117.4 (*d*); 130.0 (*s*); 138.5 (*d*); 154.2 (*s*); 206.8 (*s*). MS: 150 (99, M^+), 107 (100), 91 (62), 135 (55), 39 (54), 41 (36), 79 (32), 105 (21), 122 (19), 51 (19), 77 (18), 53 (17), 65 (15).

2.2.2. *(±)-2,5,6,6-Tetramethylcyclohexa-2,4-dienecarbaldehyde* (**26**). Following a modified method [26], NaH (80% in mineral oil; 2.3 g, 80 mmol) was washed twice with pentane, and then dry DMSO (125 ml) and **25** (11.8 g, 78.6 mmol) were added at r.t. After 10 min at r.t., trimethylsulfonium iodide (16.3 g, 80 mmol) was added in two portions, and the mixture was stirred at r.t. for 24 h. The soln. was poured into a large excess of ice/water, and the unstable epoxide was isolated by extraction with Et_2O. The dry ($MgSO_4$) Et_2O soln. was not evaporated, but slowly added at 0° to a stirred soln. of $MgBr_2$ in Et_2O (prepared from 96 mg (4 mmol) Mg and 940 mg (5 mmol) 1,2-dibromoethane in 20 ml of dry Et_2O). After 1 h at 0°, the soln. was washed with aq. $NaHCO_3$ soln., dried ($MgSO_4$), and evaporated. Bulb-to-bulb distillation (80°/2 Torr) gave 4.77 g (37%) of **26** (purity by GC 67%). A pure sample was isolated by prep. GC (*Carbowax*). IR (liq.): 3030, 2810, 2720, 1715, 820. ^{1}H-NMR: 0.98 (*s*, 3 H); 1.07 (*s*, 3 H); 1.74 (br. *s*, 6 H); 2.24 (*d*, *J* = 5, 1 H); 5.56 (br. *d*, *J* = 5.5, 1 H); 5.87 (br. *d*, *J* = 5.5, 1 H); 9.24 (*d*, *J* = 5, 1 H). ^{13}C-NMR: 18.5 (*q*); 21.9 (*q*); 23.4 (*q*); 24.7 (*q*); 36.1 (*s*); 65.5 (*d*); 119.5 (*d*); 123.4 (*d*); 127.2 (*s*); 140.6 (*s*); 200.8 (*d*). MS: 164 (30, M^+), 135 (100), 119 (38), 105 (28), 91 (19), 120 (17), 121 (15), 41 (15), 39 (14), 136 (12), 77 (12), 79 (10), 51 (6).

2.2.3. *Attempted Isomerization of* **26**. A sample of **26** was heated with Et_3N (100°/15 h, sealed tube) to attempt isomerization into **5** [27]. Only starting **26** was isolated from the mixture.

3. *Synthesis Depicted in* Scheme 2. 3.1. *(±)-(E)-3-(*cis*-2,5,6,6-Tetramethylcyclohex-2-en-1-yl)prop-2-enal* (= *10-Nor*-cis-α-*irone*, **8**). 3.1.1. *(±)-(E)-3-(*cis*-2,5,6,6-Tetramethylcyclohex-2-en-1-yl)prop-2-enoic Acid* (**27**). A soln. of (±)-*cis*-α-irone[8]) (110 g, 0.534 mol; purity 80% containing *ca.* 10% each of α-*trans*- and β-irone) in dioxane (1000 ml) was added at 0° over 3 h to a stirred soln. of NaOBr (prepared by adding Br_2 (98 ml, 1.91

[8]) Obtained by fractional distillation of commercial α-irone (*Givaudan AG*).

mol) with cooling at 0° to a stirred soln. of NaOH (203 g, 5.08 mol) in 1 l of H_2O and stirring for 1 h at 0°). Stirring was continued overnight, and the mixture was allowed to reach r.t. The excess of NaOBr was removed by heating the mixture to 40° for 2 h. The cold mixture was poured into 2 l of ice/water, and the neutral parts were removed by washing with Et_2O (4 × 1 l). Ice (500 g) was added to the alkaline aq. soln. which was acidified by careful addition of 30% aq. H_2SO_4. Crude **27** (purity 80%, yield 112 g, 100%) was isolated by repeated extraction with Et_2O (4 × 1 l) and purified by recrystallization (2 ×) from petroleum ether (50–70°) to give 60 g (67%) of pure **27**. M.p. 112–113° ([13] m.p. 115–116°). The spectral data of **27** were identical with those reported [13].

3.1.2. *(±)-(E)-3-(*cis*-2,5,6,6-Tetramethylcyclohex-2-en-1-yl)prop-2-enoyl Chloride* (**28**). A mixture of **27** (30 g, 0.144 mol) and $SOCl_2$ (15 ml, 0.208 mol) was stirred at 40° for 8 h. The excess of $SOCl_2$ was removed at 10 Torr, and the crude product was purified by bulb-to-bulb distillation (100°/0.08 Torr) to give 28.1 g (86%) of pure **28**. IR (liq.): 3020, 1755, 1615. ^{1}H-NMR: 0.74 (*s*, 3 H); 0.89 (*s*, 3 H); 0.89 (*d*, *J* = 7, 3 H); 1.49 (*m*, 1 H); 1.54 (br. *s*, 3 H); 1.76 (*m*, 1 H); 1.98 (*m*, 1 H); 2.64 (br. *d*, *J* = 11, 1 H); 5.56 (*m*, 1 H); 6.13 (*d*, *J* = 15, 1 H); 7.10 (*dd*, *J* = 15, 11, 1 H). MS: 226 (27, $M^{+\cdot}$), 121 (100), 70 (94), 93 (84), 156 (72), 41 (56), 55 (52), 39 (43), 91 (36), 77 (28), 158 (27), 42 (19), 157 (15).

3.1.3. *Catalytic Hydrogenation of* **28**. A mixture of **28** (28.0 g, 0.124 mol) and $Pd/BaSO_4$ (5%, *Fluka*, 28 g) in toluene (250 ml) was heated at reflux under vigorous stirring (*Medimex*), while a stream of H_2 (20 l/h) was passed through the suspension. After 15 h, the hydrogenation was complete, and the catalyst was removed by filtration through *Celite*. The solvent was evaporated, and the crude product was purified by bulb-to-bulb distillation (100°/0.08 Torr) to give 22.0 g (92.4%) of pure **8**, identical with the natural compound. IR (liq.): 3025, 2830, 2725, 1685, 1625. ^{1}H-NMR: 0.74 (*s*, 3 H); 0.88 (*s*, 3 H); 0.89 (*d*, *J* = 5.5, 3 H); 1.50 (*m*, 1 H); 1.54 (br. *s*, 3 H); 1.76 (*m*, 1 H); 1.98 (*m*, 1 H); 2.71 (*d*, *J* = 10.8, 1 H); 5.55 (br, 1 H); 6.19 (*dd*, *J* = 16, 7.5, 1 H); 6.71 (*dd*, *J* = 16, 10.8, 1 H); 9.56 (*d*, *J* = 7.5, 1 H). ^{13}C-NMR: *Table 2*. MS: 192 (17, $M^{+\cdot}$), 122 (100), 107 (96), 93 (78), 41 (78), 123 (59), 39 (55), 79 (53), 55 (42), 77 (32), 91 (31), 70 (31), 53 (21).

3.2. *(±)-*cis*-4-Methyl-2-(2,5,6,6-tetramethylcyclohex-2-en-1-yl)furan* (**18**). 3.2.1. *Compound.* **12**. H_2O_2 (35%, 21 ml) was added dropwise at 15° (cooling) to a stirred soln. of *(±)-cis-α*-irone[8]) (6.18 g, 30 mmol) in MeOH (100 ml) containing 3.6 ml (21.6 mmol) of 6N aq. NaOH, so that the temp. did not exceed 20°. The mixture was stirred overnight at r.t. As the conversion was only *ca.* 50%, the same amount of 6N NaOH and 35% H_2O_2 was added, and, after 24 h at r.t., a third portion (same amount) of 6N NaOH and H_2O_2 was added. The soln. was stirred at r.t. for 24 h, poured into ice/water, and extracted with Et_2O. Bulb-to-bulb distillation (100°/0.08 Torr) of the crude product gave 3.7 g (55.5%) of **12** as an oil, identical with the natural compound. IR (liq.): 1705. ^{1}H-NMR: 0.88 (*d*, *J* = 7, 3 H); 0.91 (*s*, 3 H); 1.08 (*s*, 3 H); 1.45 (*m*, 1 H); 1.60 (br. *d*, *J* = 9, 1 H); 1.63 (br. *s*, 3 H); 1.68–1.77 (*m*, 1 H); 1.88–1.98 (*m*, 1 H); 2.09 (*s*, 3 H); 2.93 (*dd*, *J* = 9, 2, 1 H); 3.22 (*d*, *J* = 2, 1 H); 5.53 (*m*, 1 H). ^{13}C-NMR: *Table 2*. MS: 222 (1, $M^{+\cdot}$), 43 (100), 70 (51), 109 (41), 41 (41), 81 (35), 55 (31), 80 (28), 39 (25), 95 (23), 79 (23), 121 (14), 91 (14).

3.2.2. *2'-Methyl-3-(2,5,6,6-tetramethylcyclohex-2-en-1-yl)-2,2'-bioxiran* (**29**) *from* **12**. A dispersion of NaH (80% in mineral oil; 129 mg, 4.3 mmol) was twice washed with pentane under Ar, and DMSO (12 ml) was added at r.t. Trimethylsulfonium iodide (918 mg, 4.5 mmol) was added in one portion, followed by addition of **12** (666 mg, 3 mmol) at r.t. After 5 h of stirring at r.t., the clear brown soln. was poured into ice/water and extrated with Et_2O. Bulb-to-bulb distillation (100°/0.08 Torr) of the crude product gave 620 mg (87.6%) of pure **29** (1:1 mixture of diastereoisomers). IR: no C=O absorption. ^{1}H-NMR: 0.87 (*d*, *J* = 6, 3 H); 0.88 (*s*, 3 H); 1.06 (*s*, 3 H); 1.35, 1.36 (2 *s*, 3 H); 1.38–1.48 (*m*, 1 H); 1.52–1.58 (*m*, 1 H); 1.70 (br. *s*, 3 H); 1.70–1.78 (*m*, 1 H); 1.87–1.97 (*m*, 1 H); 2.64–2.89 (several *m*, 4 H); 5.52 (*m*, 1 H). MS: 236 (< 1, $M^{+\cdot}$), 95 (100), 81 (58), 41 (56), 79 (47), 55 (43), 43 (42), 70 (31), 67 (31), 107 (28), 96 (27), 39 (26), 91 (22).

3.2.3. *Acid-Catalyzed Formation of* **18** *from* **29**. A soln. of the diastereoisomeric mixture **29** (118 mg, 0.5 mmol) in dry Et_2O (5 ml) was stirred at r.t. in the presence of a catalytic amount (20 µl) of $BF_3 \cdot Et_2O$. After 2 d, the soln. was washed with aq. $NaHCO_3$ soln. and evaporated. The crude product was a complex mixture of *ca.* 12 compounds (not further investigated) containing *ca.* 10% of the desired **18**. An anal. sample of **18** was isolated by prep. GC (*Carbowax*, 180°) and found to be identical with the natural compound. IR: no strong bands. ^{1}H-NMR: 0.67 (*s*, 3 H); 0.88 (*s*, 3 H); 0.89 (*d*, *J* = 6, 3 H); 1.44 (br. *s*, 3 H); 1.56 (*m*, 1 H); 1.77–1.98 (*m*, 2 H); 2.02 (br. *s*, 3 H); 3.10 (br. *s*, 1 H); 5.55 (*m*, 1 H); 5.92 (*s*, 1 H); 7.10 (br. *s*, 1 H). MS: 218 (4, $M^{+\cdot}$), 148 (100), 105 (28), 119 (25), 133 (21), 41 (19), 91 (15), 149 (12), 120 (12), 77 (11), 55 (9), 79 (8), 39 (8).

3.3. *(±)-(E)-2-Methyl-4-(*cis*-2,5,6,6-tetramethylcyclohex-2-en-1-yl)but-2-enal* (**16**). 3.3.1. *(±)-(E)-2-Methyl-4-(*cis*-2,5,6,6-tetramethylcyclohex-2-en-1-yl)but-3-enal* (**31**). A dispersion of NaH (80% in mineral oil; 2.17 g, 72.5 mmol) was twice washed with pentane under Ar to remove the mineral oil. DMSO (100 ml) was added, then trimethylsulfonium iodide (15.3 g, 75 mmol) was added in one portion. After 5 min at r.t., a soln. of

(±)-*cis*-α-irone[8]) (10.3 g, 50 mmol) in DMSO (100 ml) was added over 3 h with stirring at 15–20°. The mixture was stirred for 90 min at r.t., poured into ice/water (1000 ml), and extracted with Et_2O (3 × 500 ml). The extract was washed ($NaHCO_3$ soln.), dried ($MgSO_4$), and evaporated. Bulb-to-bulb distillation (100–120°/0.1 Torr) gave 10.5 g (95.4%) of crude **30** which was directly used for the next step. A soln. of **30** (10.5 g, 47.7 mmol) in Et_2O (20 ml) was added within 10 min at r.t. to a stirred etheral soln. of $MgBr_2$ (20.6 mmol, prepared from Mg (500 mg) and 1,2-dibromoethane (2.6 ml) in Et_2O (40 ml)). After 3 h at r.t., the mixture was washed with aq. NaCl soln., dried ($MgSO_4$), and evaporated. Bulb-to-bulb distillation (100–110°/0.2 Torr) gave 8.0 g (76%) of crude **31**, containing *ca.* 20% of **16**. A pure sample of **31** was isolated by prep. GC. IR (liq.): 3025, 2830, 2710, 1720. ^{1}H-NMR: 0.65(*s*, 3 H); 0.85(*s*, 3 H); 0.86 (*d*, *J* = 6, 3 H); 1.22 (*d*, *J* = 7, 3 H); 1.53 (br. *s*, 3 H); 1.40–1.95 (3 H); 2.39 (*m*, 1 H); 3.11 (*m*, 1 H); 5.40–5.47 (*m*, 3 H); 9.60 (*m*, 1 H). MS: 220 (2, M^+), 121 (100), 150 (67), 93 (43), 41 (17), 91 (14), 55 (14), 122 (11), 105 (11), 77 (11), 79 (10), 107 (8), 39 (8).

3.3.2. *Base-Catalyzed Isomerization of* **31** *to* **16**. Crude **31** (7.7 g, 35 mmol) was dissolved in MeOH (20 ml), and a soln. of KOH (250 mg) in MeOH/H_2O 9:1 (5 ml) was added. After stirring for 2.5 h at r.t., the mixture was diluted with ice/water and extracted with Et_2O. Bulb-to-bulb distillation of the crude product (100–110°/0.1 Torr) gave 7.1 g (92%) of crude **16** which was purified by CC (silica gel (1300 g), cyclohexane/Et_2O 7:3). Pure **16** (5.1 g, 66%) was obtained as an oil. IR (liq.): 2720, 1690, 1640. ^{1}H-NMR: 0.66 (*s*, 3 H); 0.87 (*d*, *J* = 7, 3 H); 0.97 (*s*, 3 H); 1.50 (*m*, 1 H); 1.60 (br. *s*, 3 H); 1.66–1.76 (*m*, 1 H); 1.77 (br. *s*, 3 H); 1.84–1.94 (*m*, 1 H); 2.08 (*m*, 1 H); 2.40–2.60 (*m*, 2 H); 5.45 (*m*, 1 H); 6.57 (*m*, 1 H); 9.39 (*s*, 1 H). ^{13}C-NMR: *Table 2*. MS: 220 (2, M^+), 95 (100), 137 (90), 81 (62), 41 (60), 57 (49), 39 (36), 67 (34), 55 (30), 91 (29), 79 (29), 109 (25), 43 (24).

3.4. *(±)-(*E*)-1-(*cis*-2,5,6,6-Tetramethylcyclohex-2-en-1-yl)pent-1-en-3-one* (= *10-Methyl*-cis-α-*irone*, **14**). 3.4.1. *(±)-(*E*)-1-(*cis*-2,5,6,6-Tetramethylcyclohex-2-en-1-yl)pent-1-en-3-ol* (mixture of C(3)-epimers, **32**). A soln. of **8** (22.0 g, 0.115 mol) in dry Et_2O (100 ml) was added dropwise at r.t. to a stirred soln. of EtMgBr (0.135 mol) in Et_2O (60 ml). The mixture was heated at reflux for 1 h, cooled, and poured into an excess of ice-cold aq. NH_4Cl soln. The product was isolated by extraction with Et_2O and purified by CC (500 g SiO_2, cyclohexane/Et_2O 85:15). The pure fractions (23.0 g) were purified by bulb-to-bulb distillation (120°/0.1 Torr) to give 22.2 g (87.8%) of pure **32** (epimeric mixture *ca.* 7:5). IR (liq.): 3340, 3020, 1655. ^{1}H-NMR ($CDCl_3$ + D_2O): 0.64, 0.66 (2 *s*, 3 H); 0.85–0.88 (2 *s*, 2 *d*, 6 H); 0.92, 0.94 (2 *t*, *J* = 7, 3 H); 1.45 (*m*, 1 H); 1.52, 1.55 (2 br. *s*, 3 H); 1.58–1.77 (*m*, 3 H); 1.90 (*m*, 1 H); 2.37 (br. *d*, *J* = 9, 1 H); 4.04 (*q*, *J* = 6, 1 H); 5.40–5.55 (*m*, 3 H). MS: 222 (1, M^+), 57 (100), 95 (48), 152 (47), 123 (29), 41 (29), 55 (20), 39 (14), 43 (13), 93 (12), 81 (11), 79 (10), 96 (9).

3.4.2. *Oxidation of* **32**. To a stirred mixture of **32** (20.0 g, 90 mmol) and *Celite* (22 g) in CH_2Cl_2 (200 ml), pyridinium chlorochromate (21.6 g, 100 mmol) was added in portions at 15°. The mixture was stirred at r.t. for 3 h, cyclohexane (200 ml) was added, and the insoluble part was removed by filtration through *Celite*. After evaporation of the filtrate, the crude product (20 g) was purified by flash chromatography through SiO_2 (300 g) using cyclohexane/Et_2O 80:20. The pure fractions were purified by bulb-to-bulb distillation (120°/0.1 Torr) to give 16.0 g (81%) of **14** (purity by GC 98%). IR (liq.): 3020, 1675, 1625. ^{1}H-NMR: 0.71 (*s*, 3 H); 0.86 (*s*, 3 H); 0.87 (*d*, *J* = 5.5, 3 H); 1.12 (*t*, *J* = 7, 3 H); 1.49 (*m*, 1 H); 1.52 (br. *s*, 3 H); 1.75 (*m*, 1 H); 1.95 (*m*, 1 H); 2.53 (br. *d*, *J* = 10.8, 1 H); 2.60 (*q*, *J* = 7, 2 H); 5.51 (br., 1 H); 6.13 (*d*, *J* = 16, 1 H); 6.67 (*dd*, *J* = 16, 10.8, 1 H). ^{13}C-NMR: *Table 2*. MS: 220 (25, M^+), 121 (100), 150 (88), 93 (63), 135 (43), 57 (40), 41 (31), 55 (22), 91 (21), 151 (19), 92 (18), 77 (18), 39 (17).

4. *Synthesis Depicted in* Scheme 3. 4.1. *Alkylation of a Mixture of (–)-*cis-α- *and (–)-*cis-γ-*Irone*. A 1.52M soln. of BuLi in hexane (3.6 ml, 5.5 mmol) was added under Ar at 0° to a stirred soln. of dry (i-Pr)$_2$NH (555 mg (778 µl), 5.5 mmol) in dry THF (12.5 ml). The soln. was stirred for 15 min at 10° and then cooled to –78°. HMPA (895 mg, 5 mmol) was added, and, after 30 min, a mixture (*ca.* 1:1) of (–)-*cis*-α- and (–)-*cis*-γ-irone[9]) (1.03 g, 5 mmol) in THF (12.5 ml) was added dropwise. Stirring at –78° was continued for 30 min, then MeI (887 mg, 6.25 mmol) was added. After 1 h at –78°, the mixture was stirred for 1 h at r.t. and hydrolyzed with an excess of ice-cold aq. NH_4Cl soln. The product was isolated by extraction with Et_2O and purified by bulb-to-bulb distillation (100–110°/0.05 Torr) to give 1.05 g (95%) of **14/15** (1:1), containing *ca.* 5% of the starting irones and *ca.* 10% of dialkylated irones. The mixture was separated by CC (silica gel (300 g), cyclohexane → cyclohexane/Et_2O 30:70). From the fractions containing only **14** and **15** (700 mg, 63%), pure samples of optically active **14** and **15** were isolated by prep. GC (*Carbowax*, 150°).

4.1.1. *Compound* **14**. *Peak 1*, oil. $[\alpha]_D^{20} = -99.5$ (*c* = 1.5). Spectral data are identical to those of the racemic compound (see *3.4.2*).

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[9]) For the optical rotations, see *Table 1*.

4.1.2. *Compound* **15**. *Peak 2*, oil. $[\alpha]_D^{20}$= +2.5 (*c* = 1.5). IR (liq.): 3080, 1680, 1635, 900. ^{1}H-NMR: 0.72 (*s*, 3 H); 0.86 (*d*, *J* = 6, 3 H); 0.87 (*s*, 3 H); 1.12 (*t*, *J* = 7, 3 H); 1.32 (*qd*, *J* = 12.5, 4.5, 1 H); 1.38–1.48 (*m*, 1 H); 1.52–1.59 (*m*, 1 H); 2.05–2.15 (*m*, 1 H); 2.31–2.37 (*m*, 1 H); 2.54 (br. *d*, *J* = 10, 1 H); 2.61 (*q*, *J* = 7, 2 H); 4.44 (*m*, 1 H); 4.79 (*m*, 1 H); 6.11 (*d*, *J* = 16, 1 H); 6.97 (*dd*, *J* = 16, 10, 1 H). ^{13}C-NMR: *Table 2*. MS: 220 (6, M^+), 135 (100), 57 (86), 55 (55), 163 (52), 81 (52), 137 (49), 41 (47), 83 (45), 95 (41), 107 (32), 109 (27), 43 (27).

4.2. *Preparation of (–)-***16** *and (–)-***17.** Following the method described above (*cf. 3.3.1* and *3.3.2*), a mixture (*ca.* 1:1) of (–)-*cis*-α- and (–)-*cis*-γ-irone[9]) (2.06 g, 10 mmol) was converted *via* **33** into a 1:1 mixture of optically active **16** and **17** (overall yield after distillation and CC 41%). A pure sample of each compound was isolated by prep. GC (*Carbowax*, 200°).

4.2.1. *(1*R,5S,E*)-2-Methyl-4-(2,5,6,6-tetramethylcyclohex-2-en-1-yl)but-2-enal* (**16**). *Peak 2*, oil. $[\alpha]_D^{20}$ = –10.5 (*c* = 0.5). Spectral data are identical with those described for the racemate (see *3.3.2*).

4.2.2. *(1*R,3S,E*)-2-Methyl-4-(2,2,3-trimethyl-6-methylidenecyclohex-1-yl)but-2-enal* (**17**). *Peak 1*, oil. $[\alpha]_D^{20}$ = –11.0 (*c* = 1.0). IR (liq.): 3080, 2830, 2720, 1690, 1645, 900. ^{1}H-NMR: 0.62 (*s*, 3 H); 0.87 (*d*, *J* = 7, 3 H); 1.05 (*s*, 3 H); 1.28 (*qd*, *J* = 13, 4, 1 H); 1.43–1.53 (*m*, 1 H); 1.56–1.63 (*m*, 1 H); 1.78 (br. *s*, 3 H); 1.97 (br. *d*, *J* = 11, 1 H); 2.00–2.09 (*m*, 1 H); 2.29–2.35 (*m*, 1 H); 2.41–2.51 (*m*, 1 H); 2.58–2.66 (*m*, 1 H); 4.40 (br. *s*, 1 H); 4.85 (br. *s*, 1 H); 6.46 (*t*, *J* = 6, 1 H); 9.35 (*s*, 1 H). ^{13}C-NMR: *Table 2*. MS: 220 (6, M^+), 41 (100), 55 (92), 95 (81), 81 (64), 83 (57), 93 (56), 107 (51), 67 (48), 43 (47), 91 (46), 79 (46), 121 (43).

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