Isolation and Structure Determination of the Precursors of α- and γ-Irone and Homologous Compounds from *Iris pallida* and *Iris florentina* *

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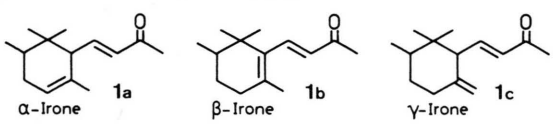
Iris florentina, Iris gemanica, Iris pallida, Irones, Iriflorental

Rhizomes of *Iris pallida* and *Iris florentina* contain – increasing on storage – violet-like smelling C_{14}-ketones (irones **1a–c**) which develop by oxidative degradation of C_{31}-triterpenoids. The structure of these precursors is reported as well as the structure of respective C_{30}-homologues.

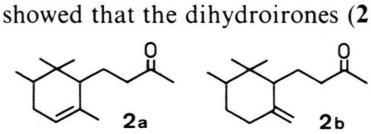
The unusual C_{31}-structures may derive biogenetically from the respective C_{30} compounds by a methylation which initiates the formation of the ring-closed irone-moiety.

Introduction

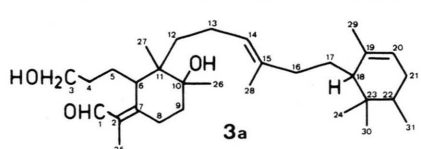
The characteristic violet-like smelling compounds of the essential oil of rhizomes of *Iris florentina* and *Iris pallida* have long been known to be the three isomeric irones (**1a–c**) [1].



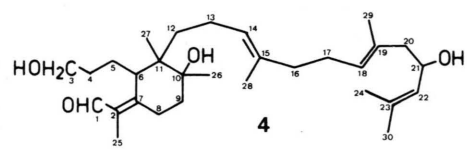
It is well established that these ketones do not occur in freshly harvested plants but develop over years by a slow process – presumably an oxidative degradation of precursor-molecules [2]. In a previous study we showed that the dihydroirones (**2a–b**) are



formed upon treatment of lipid-extracts of the rhizomes of *Iris germanica* L. with oxidative agents. The structure of their precursors was found to be α- and γ-irigermanal (**3a** and **3b**), respectively [3].



In addition to the two compounds cyclized at the C-23 terminal the open-chain homologue irido-germanal (**4**) was also identified [3].

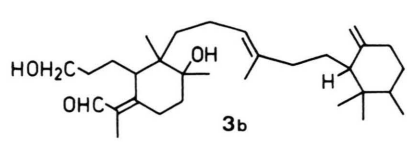


In this paper we will describe the isolation and structure determination of the precursors of α- and γ-irone (**1a** and **1c** respectively) and some of their homologues from *Iris florentina* and *I. pallida.*

Materials and Methods

Plant material

Rhizomes of *Iris pallida* were a kind gift of Dr. Steiner (Bonn) and were harvested in the garden of the Institut für Pharmakognosie, Universität Bonn, in the autumn of 1978 and 1979.



Rhizomes of *Iris florentina* were obtained by Bornträger & Schlemmer OHG, D-6521 Offstein, W.-Germany, in the fall of 1977 and 1981 as well as in the spring of 1981. If not used immediately the rhizomes were stored in a cold room (+ 4 °C).

* Professor Maximilian Steiner mit Dank und Verehrung zum 29. 4.

Reprint requests to Prof. Dr. Jaenicke.

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Extraction and isolation procedure

Extraction of 1 kg of the rhizomes yielded between 10 and 30 g of crude extract [4] which was fractionated on silicagel using a petrolether/chloroform/acetone/methanol gradient. Final purification of the compounds was achieved by low-pressure liquid chromatography on a Merck Lobar Lichroprep RP 8-column using methanol/water (80:20 or 90:10) as the eluent.

The compounds isolated amounted to 0.5% of the fresh weight of the rhizomes of *I. florentina* and to 1% in case of *I. pallida.*

Analytical Methods

The purity of the compounds was determined by HPLC using a Kontron model 200 HPLC-system equipped with a Kontron 720 LC uv-monitor and reversed phase (RP18)-columns.

Gas chromatographic separations were carried out on a Carlo Erba 2900 capillary column GC equipped with WCOT columns (50 m, 0.35 mm i.d.) coated with OV 61 and Ucon 75 H 90 000 respectively.

Mass spectra were recorded on a Finnigan MAT 4510 mass spectrometer. For the chemical ionisation (CI) and negative chemical ionisation (NCI) experiments CH_4 or NH_3 were used as reactant gases.

Except for the 400 MHz-spectra ^{1}H- and ^{13}C-NMR-spectra were obtained on a Varian EM 390 and a Varian CFT 20, respectively. Chemical shifts are reported in δ-units (ppm) relative to Me_4Si ($\delta 0$).

UV-spectra were determined on a Varian Cary 14 spectrometer and optical rotations were measured on a Zeiss 0.005° precision polarimeter.

Spectral properties

Iripallidal (**5**) formed a glasslike solid: UV-spectrum (ethanol): $\lambda_{max}(\varepsilon)$ 238 (29 500). Mass-spectrum (EI, 70 eV): 486 (M^+), 468, 450, 439, 428, 416, 398, 358, 343, 331, 313, 304. $[\alpha]_{578}^{20}$: − 7.4° (CH_2Cl_2, $c = 19.0$).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ10.25 (s, 1H), 5.96 (d, 15.5 Hz, 1H), 5.43 (m, 1H), 5.35 (dd, 10.3 Hz, 15.5 Hz, 1H), 5.16 (t, 6.8 Hz, 1H), 4.08 and 3.93 (AB-system, 11.2 Hz, 2H), 3.66 (m, 1H), 3.57 (m, 2H), 2.8−1.0 (19H), 1.85 (s, 3H), 1.64 (s, 3H), 1.50 (s, 3H), 1.32 (s, 3H), 0.85 (d, 6.8 Hz, 3H), 0.83 (s, 3H), 0.64 (s, 3H).

Decoupling experiments proved the following signals to be coupled to each other: 5.35 and 5.96, 5.35 and 2.35, 4.08 and 3.93.

Upon addition of $Eu(fod)_3$ the following shifts could be observed ($CDCl_3$, 90 MHz): 10.25 to 10.5, 4.08 to 5.23, 3.93 to 5.08, 3.66 to 4.14, 1.85 to 2.07 and 1.32 to 1.59.

^{13}C-NMR ($CDCl_3$, 400 MHz): δ190.2 (d), 162.8 (s), 137.3 (d), 134.4 (s), 134.1 (s), 133.1 (s), 129.2 (d), 128.4 (d), 121.6 (d), 76.3 (s), 68.1 (t), 62.4 (t), 56.4 (d), 46.8 (s), 42.9 (d), 38.2 (d), 37.1 (t), 35.7 (s), 35.7 (t), 32.2 (t), 32.0 (t), 27.3 (t), 26.6 (q), 26.4 (q), 24.0 (t), 23.1 (q), 21.7 (t), 15.7 (q), 14.8 (q), 12.6 (q), 11.0 (q).

From the results of NMR- and mass-spectra the molecular formula $C_{31}H_{50}O_4$ was assigned.

Oxidative degradation (see below) gave a 30% yield of α-irone (**1a**).

Iriflorental (**6**) (a glasslike solid): UV-spectrum (ethanol): $\lambda_{max}(\varepsilon)$: 237.5 (26 900). Mass-spectrum (EI, 70 eV): 486 (M^+), 468, 450, 428, 413, 331, 304. Mass-spectrum (CI, CH_4): 487 (M + 1).

High resolution mass measurement: 486.3706. $C_{31}H_{50}O_4$ requires: 486.3709 $[\alpha]_{578}^{20}$: + 47.5° (CH_2Cl_2, $c = 13.5$).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ10.25 (s, 1H), 5.93 (d, 15.5 Hz, 1H), 5.64 (dd, 15.5 Hz, 9.7 Hz, 1H), 5.15 (m, 1H), 4.72 (s, 1H), 4.48 (s, 1H), 4.07 and 3.92 (AB-system, 11.1 Hz, 2H), 3.64 (m, 1H), 3.57 (m, 2H), 2.8−1.0 (22H), 1.84 (s, 3H), 1.68 (s, 3H), 1.31 (s, 3H), 0.85 (s, 3H), 0.84 (d, 6.5 Hz, 3H), 0.64 (s, 3H).

^{13}C-NMR ($CDCl_3$, 400 MHz): δ190.2 (d), 162.9 (s), 150.6 (s), 136.8 (d), 134.1 (s), 133.1 (s), 129.6 (d), 126.6 (d), 107.8 (t), 76.3 (s), 68.1 (t), 62.3 (t), 58.3 (d), 46.8 (s), 42.9 (d), 42.3 (d), 38.7 (s), 37.1 (t), 36.5 (t), 35.6 (t), 32.2 (t), 32.2 (t), 27.7 (q), 27.3 (t), 26.3 (q), 24.0 (t), 21.7 (t), 16.1 (q), 14.3 (q), 12.6 (q), 11.0 (q).

Oxidation with $KMnO_4$/crown-ether (see below) yielded 12% of γ-irone (**1c**).

Desoxy-iripallidal (**7**) was found in trace amounts in the extracts of *I. pallida* and always came together with α-irigermanal (**3a**). We were not able to separate the two compounds. The mixture showed the following properties: Mass-spectrum (CI, CH_4): *m/e* 471 (M + 1, compound **7**). *m/e* 473 (M + 1, compound **3a**). ^{1}H-NMR-spectrum ($CDCl_3$,

90 MHz): (see Fig. 3, top). Except for the known signals for (**3a**) [3] the additional double bond showed up at 6.05 (d, 15 Hz, 1H) and 5.4 (m, 1H).

Upon oxidation with $KMnO_4$/crown ether α-dihydroirone (**2a**) and α-irone (**1a**) were found in a 9:1 ratio.

Iso-iridogermanal (**8a**) came as a glasslike solid: UV-spectrum (ethanol): $\lambda_{max}(\varepsilon)$: 256 nm (17 400). Mass-spectrum (EI, 70 eV): *m/e* 456 (M-H_2O), 446, 387, 369, 351, 337, 319, 301. (NCI, CH_4): *m/e* 474 (M^-). $[\alpha]_{578}^{20}$: + 46.7° (CH_2Cl_2, *c* = 7.6).

^{1}H-NMR-spectrum ($CDCl_3$, 400 MHz): δ10.3 (s, 1H), 5.23 (t, 7.1 Hz, 1H), 5.06 (tquint, 7 Hz, 1.4 Hz, 1H), 5.06 (t, 7 Hz, 1H), 3.91 (t, 6.6 Hz, 1H), 3.56 (t, 6.3 Hz, 2H), 3.30 (d, 10.6 Hz, 1H), 2.6–1.0 (21H), 1.82 (d, 1.2 Hz, 3H), 1.67 (d, 1.2 Hz, 3H), 1.61 (d, 1.2 Hz, 3H), 1.59 (d, 1.2 Hz, 3H), 1.53 (d, 1.2 Hz, 3H), 1.14 (s, 3H), 1.09 (s, 3H).

Decoupling experiments proved the following signals to be coupled to each other: 5.23 and 1.53, 5.06 and 1.67/1.61/1.59/2.21/2.06, 3.91 and 2.21.

Upon addition of Eu(fod)$_3$ the following shifts could be observed ($CDCl_3$, 90 MHz): 10.3 to 11.0, 5.23 to 5.90, 5.06 to 5.45, 5.06 to 5.15, 3.91 to 4.72, 3.56 to 5.45, 3.30 to 3.95, 2.57 to 3.25, 2.21 to 2.80, 2.05 to 2.17, 1.82 to 2.17, 1.67 to 1.74, 1.61/1.59 to 1.82/1.65, 1.53 to 1.95, 1.14 to 1.35 and 1.09 to 1.40.

^{13}C-NMR-spectrum ($CDCl_3$, 400 MHz): α190.2(d), 163.4 (s), 138.1 (s), 137.1 (s), 133.0 (s), 131.4 (s), 125.5 (d), 124.2 (d), 120.1 (d), 76.8 (d), 74.8 (s), 62.7(t), 44.8 (s), 43.6 (d), 39.8 (t), 37.0 (t), 37.0 (t), 34.2 (t), 32.6 (t), 26.8 (t), 26.6 (t), 26.1 (q), 25.6 (q), 23.1 (t), 21.8 (t), 17.9 (q), 17.7 (q), 16.3 (q), 11.8 (q), 10.9 (q). Upon oxidation with $KMnO_4$/crown ether 6-methyl-5-heptene-2-one (**9**) and 6,10-dimethyl-undeca-5,9-diene-2-one-3-ol (**10**) are found (see below).

From the spectral properties the molecular formula $C_{30}H_{50}O_4$ could be assigned.

21-Desoxy-iridogermanal (**8b**) (glasslike solid): UV-spectrum (ethanol): $\lambda_{max}(\varepsilon)$: 255 nm (11 250). Mass-spectrum (EI, 70 eV): *m/e* 458 (M^+), 440, 426, 415, 397, 371, 357, 315, 308, 303 (CI, CH_4): *m/e* 459 (M + 1). (NCI, CH_4): *m/e* 458 (M^-). $[\alpha]_{578}^{20}$: + 34.4° (CH_2Cl_2, *c* = 0.9).

^{1}H-NMR-spectrum (CDI_3, 400 MHz): δ10.3 (s, 1H), 5.09 (t, 4.5 Hz, 1H), 5.07 (t, 4.5 Hz, 1H), 4.97 (t, 5 Hz, 1H), 3.6 (t, 5.4 Hz, 2H), 3.32 (m, 1H), 2.6–1.0 (22H), 1.83 (3H), 1.67 (3H), 1.59 (3H), 1.57 (3H), 1.52 (3H), 1.16 (3H), 1.09 (3H).

10-Desoxy-iridogermanal (**8c**) was isolated as a glass-like solid: UV-spectrum (ethanol): $\lambda_{max}(\varepsilon)$: 256 nm (13 500). Mass-spectrum (EI, 70 eV): *m/e* 440 (M-H_2O), 374, 356, 331, 317, 313, 304. (NCI, CH_4): *m/e* 458 (M^-). $[\alpha]_{578}^{20}$: + 33.4° (CH_2Cl_2, *c* = 4.2).

^{1}H-NMR-spectrum ($CDCl_3$, 90 MHz): δ10.2 (s, 1H), 5.12 (m, 2H), 4.96 (t, 7.5 Hz, 1H), 4.38 (dt, 6.9 Hz, 7.5 Hz, 1H), 3.57 (t, 6 Hz, 2H), 3.38 (t, 8.4 Hz, 1H), 2.8–1.0 (20H), 1.80 (3H), 1.70 (3H), 1.67 (3H), 1.62 (3H), 1.50 (3H), 0.95 (3H), 0.82 (d, 6.3 Hz, 3H).

^{13}C-NMR-spectrum ($CDCl_3$, 400 MHz): δ190.0 (d), 163.6 (s), 134.7 (s), 134.4 (s), 133.1 (s), 131.4 (s), 128.3 (d), 127.5 (d), 124.7 (d), 65.7 (d), 62.5 (t), 48.1 (t), 43.2 (d), 40.0 (s), 39.4 (t), 35.6 (d), 31.7 (t), 31.3 (t), 30.4 (t), 27.3 (t), 26.3 (t), 25.7 (q), 24.1 (q), 23.9 (t), 21.0 (t), 18.1 (q), 16.1 (q), 15.7 (q), 15.2 (q), 10.7 (q).

Oxidative degradations

The oxidative cleavage of the compounds was carried out following the procedure of Sam and Simmons [5]: 0.7 mmol of the triterpenoid was dissolved in 40 ml of benzene and 36 mg (0.097 mmol) of dicyclohexano-18-crown-6 (EGA Chemie GmbH, D-7924 Steinheim, W.-Germany) was added. Within 8 h 460 mg (2.91 mmol) $KMnO_4$ was added in portions at room-temperature. The reaction mixture was stirred over-night, the benzene was distilled off, and after filtration the residue was chromatographed on silicagel using a pentane/pentane-ether (9:1) gradient as the eluent.

If possible, the compounds isolated were compared with commercially available substances by GC/MS and retention-indices:

Natural *Iris*-oil *(Essence Iris Absolue)* was obtained by P. Kaders, Hamburg, W.-Germany, and consisted of 60% α-irone (**1a**) and 40% of the γ-isomer (**1c**), which were separated by preparative GLC (column: 2.5 m × 4 mm i.d., 20% PEG 4M on Chromosorb P, 60–80 mesh, 175 °C).

6-Methyl-5-heptene-2-one (**9**) was obtained by EGA-Chemie GmbH, D-7924 Steinheim, W.-Germany.

For the synthesis of α-dihydroirone (**2a**) see [3]. 6,10-Dimethyl-undeca-5,9-diene-2-one-3-ol (**10**) was identified by its mass-spectrum (EI, 70 eV): *m/e* 210 (M^+), 192, 177, 167, 165, 149, 141, 137, 123, 109, 95, 81, 74, 69, 55, 53, 45, 42, 40, 38.

Upon addition of N-methyl-N-trimethyl-silyl-trifluor-acetamide (MSTFA) the trimethylsilylether was formed. Mass-spectrum (EI, 70 eV): *m/e* 282 (M^+), 264, 239, 192, 169, 157, 155, 149, 146, 130, 107, 93, 81, 73, 69, 45, 43, 41.

Oxidation of iso-iridogermanal (**8a**) *with* $CrO_3 \cdot 2Pyr$. Dipyridine-chromium(VI)-oxide oxidation [6] of **8a** was carried out as follows: 0.45 ml pyridine were dissolved in 10 ml CH_2Cl_2. 279 mg (2.79 mmol) CrO_3 was added, and the solution was stirred at room-temperature for 15 min. A solution of 132 mg (0.278 mmol) **8a** was then added in one portion. After stirring at room-temperature for additional 30 min the CH_2Cl_2 was evaporated *in vacuo*. The residue was eluted with ether and the product purified by low-pressure liquid chromatography on a reversed phase column using methanol/water (80:20) as the eluent to yield 17.8 mg (13.6%).

The product showed the following spectral properties: UV-spectrum (ethanol): $\lambda_{max}(\varepsilon)$: 240 nm (11 000), 255 nm (sh). Mass-spectrum (EI, 70 eV): *m/e* 470 (M^+), 455, 452, 397, 333, 315, 306, 301.

In the ^{1}H-NMR-spectrum ($CDCl_3$, 90 MHz) a new aldehyde signal appeared at δ 9.71 and one of the olefinic protons was shifted to δ 6.40.

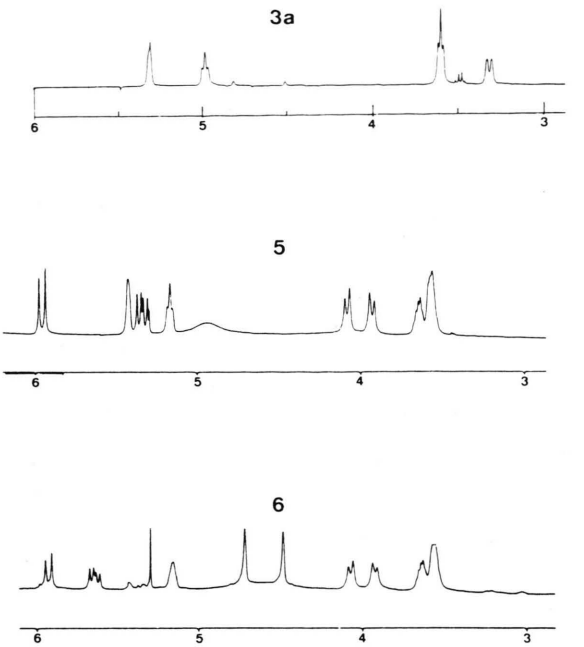


Fig. 1. 400 MHz-^{1}H-NMR spectra of α-irigermanal (**3a**), iripallidal (**5**) and iriflorental (**6**).

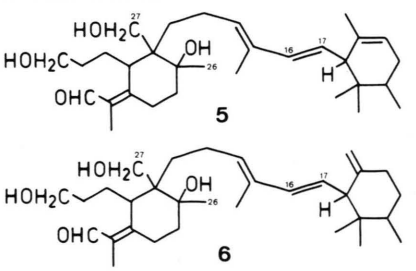
Results and Discussion

Two compounds were isolated from *Iris pallida* as well as *I. florentina* and were named iripallidal (**5**) and iriflorental (**6**) after their main-occurrence in the respective species. Already on contact with air iripallidal releases α-irone (**1a**) and iriflorental γ-irone (**1c**) as opposed to the irigermanals (**3a, 3b**) which are quite stable under these conditions.

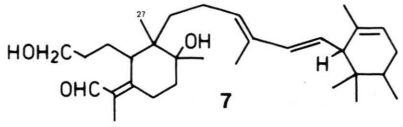
From their spectral properties it was evident that the irone-precursors isolated had to be similar in their overall structure to the substances from *I. germanica* L. However, in addition, in both iripallidal and iriflorental one double-bond and one extra hydroxy-group had to be present since ^{13}C- and mass-spectra indicated a formula of $C_{31}H_{50}O_4$. As mentioned above on oxidation the compounds yield α- or γ-irone (**1a** or **1c**) respectively; thus the additional double-bond has to be in the irone-moiety between C-16 and C-17. This fits perfectly with the ^{1}H-NMR signals for the protons of this double bond at δ 5.95 and 5.35 (Fig. 1, middle: iripallidal) or δ 5.93 and 5.64 (Fig. 1, bottom: iriflorental). The coupling of the two protons (J = 15.5 Hz) indicates an E-geometry.

Compared to the irigermanals the signal for one methyl-group is missing in the NMR-spectra of iripallidal and iriflorental which, instead, show an AB-system for two protons at δ 4.08 and 3.93 (4.07 and 3.92 respectively, see Fig. 1, middle and bottom). Clearly one methyl-group has been oxidized to a CH_2OH-group.

Since the methyl-group in β-position to the aldehyde-function still is present, either C-26 or C-27 had to bear the hydroxy-function. As all attempts of a glycol-cleavage failed which should have resulted in the formation of a keto-group in C-10, in case C-26 was the CH_2OH, we assigned it to C-27. Consequently iripallidal has structure **5** and iriflorental structure **6**.



Extracts from *Iris pallida* contained in trace amounts a compound which was identical with iripallidal except for the missing hydroxy-group in C-27 (desoxy-iripallidal (**7**)).



7

Part of the 90 MHz-spectrum of **7** is shown in Fig. 3 (top).

From their ^{13}C- and mass-spectra the two other compounds isolated from *I. pallida* as well as *I. florentina* extracts appear to be isomers of iridogermanal (**4**). As shown in Fig. 2, the difference between **4** (top) and iso-iridogermanal (**8a**) (middle) is in the position of the secondary hydroxy-group in the side-chain.

The signal at δ 3.91 indicates that the proton next to the OH is coupled only to a CH_2 and not to an olefinic proton as in iridogermanal. Thus five possible positions had to be considered for the hydroxy-group viz. C-8, C-9, C-12, C-16 or C-20. When recorded in presence of $Eu(fod)_3$, the proton-NMR of **8a** results in a large shift of one olefinic proton from δ 5.23 to δ 5.9 and a somewhat smaller shift of another olefinic proton from δ 5.06 to 5.45. Therefore only C-16 or C-20 could bear the oxygen-function. This was confirmed by oxidation of **8a** with CrO_3-bipyridyl-complex [6]. A dramatic shift of the NMR-signal at 5.23 to 6.40 proved the appropriate proton to be now in β-position of an α, β unsaturated carbonyl-group: the alcohol function had been oxidized to a ketone. Final confirmation that C-16 was the CHOH-group was achieved by oxidative degradation of **8a** with $KMnO_4$, as 6-methyl-5-heptene-2-one (**9**) and 6,10-dimethyl-undeca-5,9-diene-2-one-3-ol (**10**) were formed.

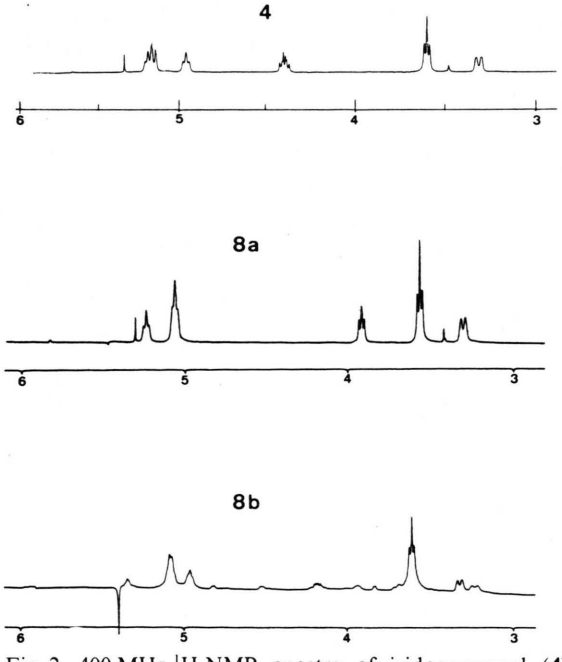


Fig. 2. 400 MHz-^1H-NMR spectra of iridogermanal (**4**), iso-iridogermanal (**8a**) and 21-desoxy-iridogermanal (**8b**).

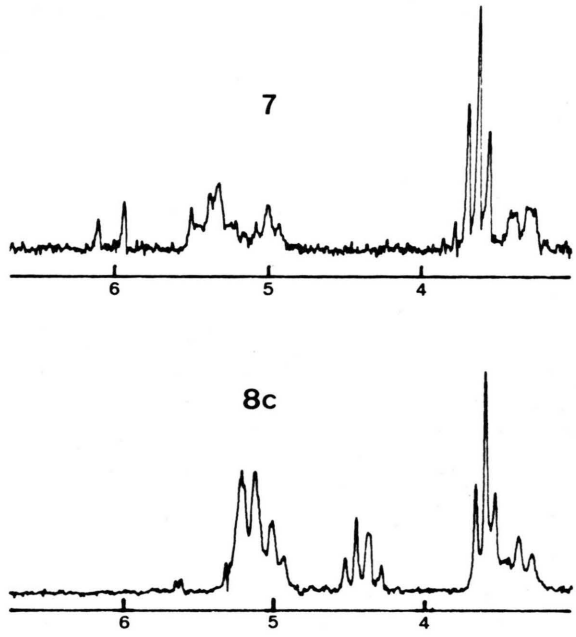
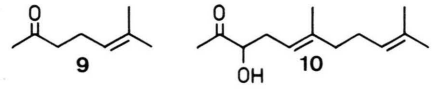
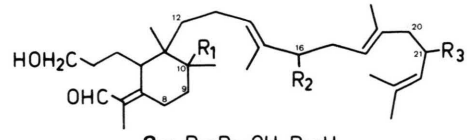


Fig. 3. 90 MHz-^1H-NMR spectra of desoxy-iripallidal (**7**) and 10-desoxy-iridogermanal (**8c**).



Thus the structure of iso-iridogermanal has been established as **8a**.



8a: $R_1 = R_2 = OH$; $R_3 = H$
8b: $R_1 = OH$; $R_2 = R_3 = H$
8c: $R_1 = R_2 = H$; $R_3 = OH$

Table I. Occurrence of triterpenoids in different *Iris* species.

	Main-products (> 10%)	Side-products (1 – 10%)	Traces (< 1%)
I. germanica	**3a, 3b, 4**	**8b, 8c**	**5, 6**
I. pallida	**5**	**8a, 3a**	**7**
I. florentina	**6**	**8a**	**5, 8b**

The other isomer of **4** and **8a** is the desoxy-compound **8b**. The ^{1}H-NMR (Fig. 2, bottom) shows the absence of any OH in the side chain. All other signals of **4** are still present. Furthermore the mass-spectrum proves the absence of oxygen by the molecular ion *m/e* 458, 16 mass units less than the M^+ of **4** and **8a** (*m/e* 474).

The same molecular weight and elemental composition has been found for an additional isomer of iridogermanal which was isolated in trace amounts from rhizomes of *Iris germanica* L. As can be taken from Fig. 3 by the signal at δ 4.38 (Fig. 3, bottom), this compound still possesses the OH-function in C-21. Since the terminal CH_2OH (δ 3.57) was still present too, the oxygen at C-10 had to be missing. Thus the structure of 10-desoxy-iridogermanal is **8c**.

Table I shows the occurrence of all triterpenoids isolated from the three species. It is evident that the distribution is quite characteristic and may be used for chemotaxonomic purposes of *Iris* species. We found a seasonal dependence of isomer distribution only in the case of *I. germanica* as reported previously [3]. A precursor for β-irone (**1b**) was not found in any of the species. We therefore assume that β-irone derives by isomerization of the α- or γ-isomer.

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