Isolation and Structural Determination of a New Methylated Triterpenoid from Rhizomes of *Iris versicolor* L.

Wolfgang Krick, Franz-Josef Marner, and Lothar Jaenicke

Institut für Biochemie der Universität zu Köln, An der Bottmühle 2, D-5000 Köln 1, Bundesrepublik Deutschland

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*A mono cyclic C31-triterpenoid was isolated from rhizomes of *Iris versicolor* L. Its structure was elucidated as 12 by spectroscopy combined with oxidative degradation. The identity of the degradation-products was proven by comparison with synthetic references.*

**Introduction**

The two isomeric irones 1a – 1b are constituents of the essential oil of *Iris florentina* and *Iris pallida* [1].

![Irone structures](image)

In a previous communication we showed that these two irones develop on oxidative cleavage of the methylated triterpenoids iripallidal (2a) or its isomer iriflorental (2b) respectively [2].

![Triterpenoid structures](image)

Their possible precursor on the biogenetic pathway from squalene is the C30-compound isoiridogermanal (3) which was found in rhizomes of *Iris pallida* as well as *Iris florentina* [2].

**Materials and Methods**

**Plant material**

Rhizomes of *Iris versicolor* L. were obtained by Bornträger & Schlemmer OHG, D-6521 Offstein, W.-Germany in May 1982.

**Extraction and isolation procedure**

Extraction of 950 g of the rhizomes with methanol and chloroform as described in [3] yielded 54 g of crude extract 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 a methanol/water (80/20)-methanol gradient as the eluent [3].

Iriversical amounted to 0.2% of the fresh weight of the rhizomes. Isoiridogermanal (3) and 21-desoxy-iridogermanal [2] were found in trace amounts. The triterpenoids form colorless, lacquerlike solids.

**Analytical methods**

The purity of the compounds isolated was determined by HPLC on a Kontron Model 200 HPLC-system equipped with a Kontron model 720 uv-monitor and reversed phase (RP 18) columns.
For the analytical gas-chromatography a Carlo Erba 2900 capillary gas-chromatograph equipped with WCOT glass-capillary columns (50 m x 0.35 mm) coated with OV 61 and Ucon 75 H 90000 respetively was used.

Mass spectra were recorded using a Finnigan MAT 4510 GC/MS-system.

Proton-NMR-spectra were obtained on a Varian EM 390. Chemical shifts were reported in δ-units (ppm) relative to Me$_4$Si (δ0).

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

**Spectral properties of iriversical (12)**

UV spectrum (ethanol): $\lambda_{max}$ (ε): 256 nm (15 200).


Mass spectrum (Cl, CH$_4$): 473 (M+1$^+$). [α]$^1$H$_2$: +37° (CH$_2$C$_12$, c 5.2).

'H-NMR spectrum (CDC$_1$_3, 90 MHz): δ10.25 (s, 1 H), 5.09 (m, 1 H), 4.98 (t, 6.8 Hz, 1 H), 4.71 (s, 1 H), 4.66 (s, 1 H), 3.60 (t, 6.3 Hz, 2H), 3.30 (dm, 11 Hz, 1H), 1.60 (s, 3H), 1.52 (s, 3H), 1.18 (s, 3H), 1.09 (s, 3H), 1.02 (d, 7.2 Hz, 6H).

'C-NMR spectrum (CDC$_1$_3, 400 MHz): δ190.1 (d), 163.3 (s), 155.9 (s), 135.3 (s), 134.9 (s), 132.9 (s), 124.0 (d), 123.4 (d), 106.1 (t), 74.9 (s), 62.7 (t), 44.7 (s), 43.3 (d), 39.5 (t), 38.4 (t), 37.2 (t), 36.8 (t), 33.7 (d), 33.0 (t), 32.5 (t), 26.6 (t), 26.4 (t), 26.0 (q), 23.8 (t), 22.0 (t), 21.8 (q), 21.8 (q), 17.8 (q), 16.0 (q), 15.9 (q), 10.8 (q).

Oxidation of iriversical (12) with KMnO$_4$/crownether

A solution of 9.5 mg (0.06 mmol) KMnO$_4$ and 29.6 mg (0.06 mmol) dicyclohexano-18-crown-6 in 3 ml benzene was added dropwise at room-temperature to a solution of 9.6 mg (0.02 mmol) iriversical (12) in 2 ml benzene [4]. The reaction mixture was stirred at room-temperature for 6 h. After filtration the products 4 and 5 were identified by gas-chromatographic and mass-spectrometric comparison with synthetic references (see below).

6-Methylheptane-2,5-dione (4)

Mass spectrum (EI, 70 eV): m/e 142 (M$^+$), 127, 99, 98, 71, 57, 55, 43, 41, 39.

Kovâts-indices: Ucon 75 H 90000 (130 °C): 1459.8 ± 0.6, OV 61 (110 °C): 1084.8 ± 0.4.

5-Methylene-6-methylheptan-2-one (5)

Mass spectrum (EI, 70 eV): m/e 140 (M$^+$), 125, 122, 107, 97, 83, 82, 81, 79, 71, 69, 67, 58, 55, 54, 43, 41, 39.

Kovâts-Indices: Ucon 75 H 90000 (110 °C): 1292.4 ± 0.4, OV 61 (110 °C): 1044.9 ± 0.3.

6,10-Dimethyl-9-methylene-5-undecen-2-one (6)

Mass spectrum (EI, 70 eV): m/e 208 (M$^+$), 190, 175, 165, 150, 135, 123, 107, 95, 83, 82, 81, 79, 76, 55, 53, 43, 41, 39.

**Synthesis of 6-Methylheptane-2,5-dione (4) and 5-methylene-6-methylheptan-2-one (5)**

23.46 g 6-methyl-5-hepten-2-one (0.186 mol) was added to a solution of 0.193 mol perbenzoic acid in 275 ml ether at 0 °C. After standing at 0 °C for 16 h the solution successively was washed with 10% aqueous NaOH and water. The epoxide 8 was isolated in 63% yield (16.75 g).

Mass spectrum (EI, 70 eV): m/e 142 (M$^+$), 127, 114, 109, 100, 99, 85, 84, 83, 72, 71, 59, 58, 57, 55, 43, 41, 39.

'H-NMR spectrum (CDC$_1$_3, 90 MHz): δ2.73 (t, 7.2 Hz, 1H), 2.60 (t, 8.1 Hz, 2H), 2.18 (s, 3H), 1.80 (m, 2H), 1.30 (s, 3H), 1.27 (s, 3H).

5,6-Epoxy-6-methylheptan-2-one (8)

16.75 g epoxide 8 (0.12 mol) dissolved in 100 ml ether was added dropwise at such a rate that the temperature of the solution was maintained at 30 °C. After standing for an hour at room-temperature the reaction mixture was hydrolyzed with wet ether and water at 0 °C.

Extraction with ether, drying over MgSO$_4$ and evaporation of the solvent yielded 16.3 g (94%) of a mixture of the 2,5- and the 2,6-diol (9 and 9a) in a
1:2 ratio. The crude mixture was used for the next step without further purification.

Mass spectrum (EI, 70 eV) 9: m/e 128 (M-18)+, 113, 103, 95, 86, 85, 73, 71, 69, 67, 58, 57, 56, 55, 45, 43, 41, 39.

Mass spectrum (EI, 70 eV) 9a: m/e 131 (M-15)+, 113, 103, 95, 84, 77, 73, 71, 69, 59, 58, 57, 56, 55, 45, 42, 41, 39.

'H-NMR-spectrum (CDCl₃, 90 MHz) 9 and 9a: δ 3.78 (m), 3.32 (m), 1.85–1.30 (m's), 1.50 (s), 1.24 (s), 1.20 (d, 7 Hz), 0.93 (d, 8 Hz).

6-Methylheptane-2,5-dione (4)

To a solution of CrO₃-pyridinium-complex prepared from 103.9 g pyridine (1.32 mol) and 66 g CrO₃ (0.66 mol) in 500 ml CH₂Cl₂ according to [6] a solution of 8 g of the diol-mixture 9 and 9a (54.8 mmol) in 50 ml dichloromethane were added at once. The mixture was stirred for 30 min. The solution was decanted, and the brown residue was washed with 50 ml CH₂Cl₂. After evaporating the CH₂Cl₂ the residue was dissolved in ether. Insoluble material was filtered off and the filtrate was evaporated again.

The crude 4 was purified by chromatography on silicagel using a petroleum/ether-gradient as the eluent. Yield: 1.4 g (57.5% based on 9. Mass spectrum (EI, 70 eV): see above.

Kováts-indices: Ucon 75 H 90000 (130 °C) 1459.8 ± 0.7, OV 61 (110 °C) 1084.0 ± 0.6.

'H-NMR spectrum (CDCl₃, 90 MHz): δ 2.70 (s, 1 H), 2.60 (m, 1 H), 2.18 (s, 4 H), 1.10 (d, 8 Hz, 6 H).

2-(1,3-Dioxolane)-6-methylheptan-5-one (10)

A solution of 810 mg of the diketone 4 (5.7 mmol), 0.39 g 1,2-dihydroxyethane (6.27 mmol) and 40 mg p-toluenesulfonic acid in 20 ml CHCl₃ was refluxed at the water separator for 2 h.

The solution was washed with 2 N NaOH and water, dried over MgSO₄, and the solvent was evaporated to give a 3:1 mixture of 10 and its isomeric 5-dioxolane 10a. The mixture was used without further purification for the subsequent Wittig-reaction.

Mass spectrum (EI, 70 eV) 10: m/e 171 (M-15)+, 143, 126, 111, 99, 87, 71, 55, 43.

Mass spectrum (EI, 70 eV) 10a: m/e 143 (M-43)+, 126, 115, 99, 71, 55, 43, 41.

5-Methylene-6-methylheptan-2-one (5)

A slurry of 8.9 g methyl-triphenylphosphonium-iodide (22 mmol) in 100 ml THF was treated at room-temperature with 42.3 ml of a 0.53 N solution of n-butyllithium in pentane (22.4 mmol). After 15 min at room-temperature a solution of 0.82 g of the ketal-mixture 10 and 10a in 50 ml THF was added. After 3 h the reaction-mixture was hydrolyzed with 50 ml water and extracted with ether. The organic phase was dried over MgSO₄ and evaporated.

Mass spectrum (EI, 70 eV) 11: m/e 169 (M-15)+, 139, 133, 122, 107, 99, 87, 81, 67, 55, 43.

The crude product was dissolved in 50 ml acetone, 5 ml H₂SO₄ are added, and the solution was stirred at room-temperature for 3 h.

The acetone was evaporated and the residue extracted with ether. After drying over MgSO₄ and evaporation of the solvent the residue was chromatographed on silicagel using a petroleumether/ether-gradient. Final purification of 5 was achieved by preparative GC (2 m x 4 mm 15% DEGS on Chromosorb 60–80 mesh). A total of 9 mg of the ketone 5 was obtained. Mass-spectrum (EI, 70 eV): see above.

Kováts-indices: Ucon 75 H 90000 (110 °C) 1293.7 ± 0.9, OV 61 (110 °C) 1044.4 ± 0.3.

'H-NMR spectrum (CDCl₃, 90 MHz): δ 4.80 (s, 1 H), 4.62 (s, 1 H), 2.7–2.2 (m, 5 H), 2.17 (s, 3 H), 1.00 (d, 8 Hz, 6 H).

Results and Discussion

As seen from NMR- and mass-spectra, iriversical has the formula C₃₁H₅₂O₃. Comparison of the NMR-data of this triterpenoid with the compounds previously isolated from Iris rhizomes proved the irone-moiety to be missing but the substituted cyclohexane-system at the other end of the molecule to be present. In contrast to isoiridogerinan 3, the open chain end of the molecule did not bear any hydroxy-group but, instead, one additional carbon. Three double-bonds had to be present in that part of the molecule. Two of these double-bonds are trisubstituted, one substituent being a methyl-group (δ 1.53 and δ 1.61 respectively). The third double-bond apparently was an olefinic methylene-group, the protons of which showed up at δ 4.66 and δ 4.71 in the 'H-NMR.

The appropriate ¹³C-NMR-signals are found at δ 106.1 (t) and δ 155.9 (s).
The isopropylidene-group of isoiridogermanal 3 is saturated in this compound because the methyl-groups at δ1.02 are coupled to a methine-group at δ2.1.

Oxidative degradation of iriversical with KMnO₄/crown-ether resulted in the formation of three compounds. Two of them were identified as 6-methylheptane-2,5-dione 4 and 5-methylene-6-methylheptan-2-one 5 by GC/MS and comparison with synthetic material.

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The third oxidation product presumably is 6,10-dimethyl-9-methylen-5-undecen-2-one 6 since the mass-spectrum shows a molecular ion at m/e 208. No further attempts have been made to verify this structure.

The synthesis of the diketone 4 and the ketone 5 followed the route outlined in scheme 1.

Epoxidation of 6-methyl-5-hepten-2-one 7 followed by reduction of the epoxide 8 with AlH₃ gave a mixture of the two diols 9 and 9a. Oxidation of the diol mixture yielded the diketone 4 which was easily separated from unwanted products and proved identical with the corresponding oxidation-product from iriversical.

Upon condensation of the diketone 4 with dihydroxyethane the desired dioxolane 10 was formed in favour of the product 10a. Wittig-reaction of 10 and 10a with triphenylphosphonium-methylene and subsequent hydrolysis of the dioxolanes 11 and 11a yielded a mixture of the two ketones 5 and 5a which were separated by preparative GLC.
