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AN EPOXIDIZED IRIDAL FROM *IRIS GERMANICA* VAR "ROCOCO"

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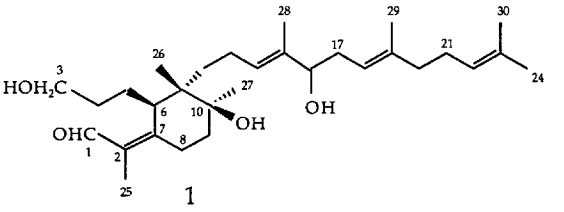
Key Word Index—*Iris germanica*; Iridaceae; iridals; triterpenoids.

Abstract—A new iridal has been isolated from rhizomes of *Iris germanica* var. "Rococo". On the basis of spectral data, its structure was established as 18,19-epoxy-10-deoxyiridal (**5**). This compound is the first epoxidized iridal discovered so far.

INTRODUCTION

Iris plants contain a family of unusual triterpenoids named iridals [1]. Since 1982 around 30 members of this family and their esters with fatty acids have been reported [2]. Some of the compounds are oxidatively cleaved to give the irones, which are responsible for the fine violet-like scent of iris oil, widely used in perfumery. The iridals seem to play as constituents of cell membranes a role comparable to that of sterols [3–5]. The present paper describes the isolation and structure elucidation of a new monocyclic iridal which is epoxidized in the side chain.



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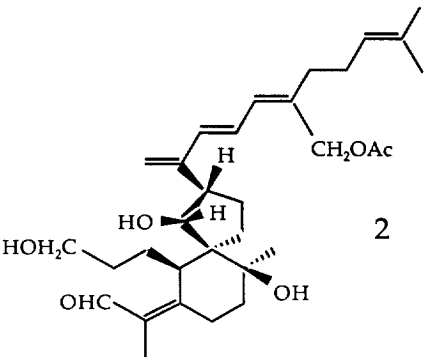

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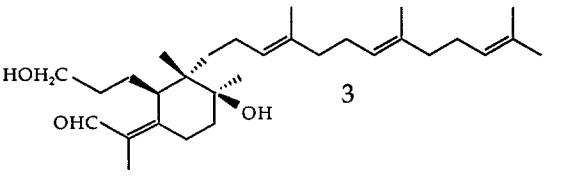

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RESULTS AND DISCUSSION

The lipid extract of rhizomes of *Iris germanica* L. var "Rococo", a horticultural hybrid, was found to contain four main unesterified iridals, three of which were identified by comparison with authentic standards as 16-hydroxyiridal (**1**) (approx. 20% of the free iridals), 29-acetoxyspiroiridal (**2**) (7%) and iridal (**3**) (53%). The fourth triterpenoid, amounting to 13% of the total of iridals, was a new compound. It was purified by silica gel and RP chromatography and its structure was elucidated by spectroscopic means.

The UV spectrum with a λ_{max} at 254 nm indicated the presence of an α,β-unsaturated carbonyl group, whereas apparently no conjugated diene or triene moieties were present in the side chain, as found in the cycloiridals or iridotrienes [2]. The mass spectra showed ions at m/z 459 (PCI), 457 (NCI) and 458 (EI), respectively, indicating a M_r of 458.

For the determination of the structure the ^{1}H- and ^{13}C NMR spectra were recorded and ^{1}H,^{1}H-COSY, ^{13}C,^{1}H-correlation and ^{13}C,^{1}H-long range experiments

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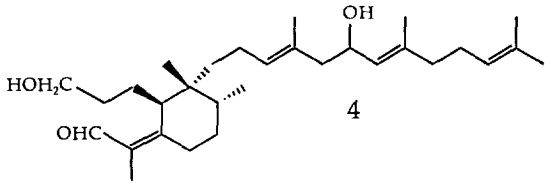
were carried out. In conjunction with the mass spectral data these established a molecular composition of $C_{30}H_{50}O_3$.

The NMR spectra clearly indicated the presence of a 10-deoxyiridal skeleton, since besides the typical signals at δ_H 10.18 and δ_C 189.9 for the aldehyde function and the ^{13}C resonances at δ 133.3 and 163.3 for the carbons of the adjacent exocyclic double bond a doublet of the C-27 methyl group at δ_H 0.80 was seen. H-10 gives rise to a resonance at δ_H 1.88. Also the other ^1H- and ^{13}C-NMR signals of the ring system compared well with the corresponding data recorded for 10-deoxy-17-hydroxyiridal **4** [6]. In contrast to **4**, the homofarnesyl side chain of the new iridal has only two double bonds and instead of one, two neighbouring C-atoms are bound to an oxygen, which can be seen by their resonances at δ_C 63.4 and 60.8, respectively. The former bears one proton (δ_H 2.65), whereas the latter is a quaternary carbon, thus indicating that one of the terpenoid double bonds has been epoxidized.



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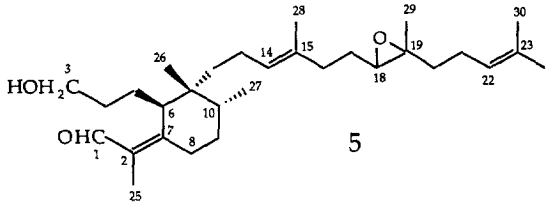
The 2D NMR experiments helped in locating the epoxide moiety. The olefinic proton at δ 5.05 showed allylic coupling with two methyl groups at δ 1.58 and 1.66 and cross peaks in the long range spectrum with the corresponding ^{13}C resonances at δ 17.7 and 25.7, this meant that the double bond at the end of the side chain between C-22 and C-23 still had to be present. The same olefinic proton showed vicinal coupling to a CH_2 group at δ_H 2.04 and δ_C 23.8, which in turn was connected to a CH_2 group (1.6/1.38, 38.8) and correlated in the long range spectrum with the quaternary epoxide carbon at δ 60.8. Therefore, the epoxide was located in the C-18/C-19 position and the compound is 18,19-epoxy-10-deoxyiridal (**5**).



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From biosynthetic considerations and from the identical NMR data we have assigned to **5** the same 6S,10R,11R-configuration as found for other deoxyiridals [2, 6]. The stereochemistry at the epoxide ring still has to be determined.

EXPERIMENTAL

General

HPLC: Gilson apparatus consisting of 2 Gilson 305 and 302 pumps (25 SC heads), a Gilson 112 UV-Vis detector. Columns: semi preparative Hibar Lichrospher RP-18, 100 Å, 10 μm, 250 × 25 mm (Merck, Germany) and analytical Kromasil, C18, 5 μm, 100 Å, 250 × 4.6 mm (Touzart & Matignon, France). MeOH–H_2O gradient from (4:1) during 2 min to MeOH in 20 min and again 30 min with MeOH. UV detection at 254 nm. MS: Finnigan-MAT 4510 GC/MS, solid probe (EI: 70 eV), CI (NH_3): Hewlett Packard 5989A; UV: Hitachi U-2000 spectrophotometer (MeOH). $[\alpha]_{546}$: Zeiss 0.005° precision polarimeter, in CH_2Cl_2 (c in g/100 ml). NMR: Bruker AM-300 (^1H: 300 MHz, ^{13}C: 75 MHz).

Plant material

Iris germanica L. var. *Rococo* was obtained from the *Iris* producer "Les *Iris* de Thau" 14, Rue des Logis, Loupian, 34140 Mèze, France and cultivated in the field of the University of Montpellier II.

Extraction and isolation

The rhizomes were cleaned under tap water, cut into pieces and ground in a grinder (Janke & Kunkel, model A10). The mash (fr. wt 250 g) was deposited into cellulose extraction thimbles (Whatman, 41 × 123 mm) and extracted three times with EtOH–H_2O (7:3) at room temp. in a Tecator apparatus. The combined extracts were filtered through Analypore EC membranes (0.45 μm, Nalgene filtration system) and the solvent removed *in vacuo*. H_2O (100 ml) was added and the resulting suspension was washed four times (4 × 100 ml) with Et_2O. The combined organic phases were concentrated to dryness *in vacuo* at 40° to give 5 g of crude extract, which was subjected to CC on silica gel 60 (0.063–0.200 mm, Merck) using $CHCl_3$–MeOH (49:1). The iridal **5** was eluted under these conditions prior to all other iridals. Subsequently, the product was purified by two consecutive HPLC separations. The first chromatography was carried out on a semi prep. column and the final purification achieved on an analytical column (see above for conditions).

(6*S*,10*R*,11*R*)-18,19-Epoxy-10-deoxyiridal (**5**).

UV λ_{max} nm (ε): 254 (11 000); $[\alpha]_{546}^{20} = +24$ (c = 0.125); EIMS *m/z* (rel. int.) 458 $[M]^+$ (1), 440 $[M-H_2O]^+$ (1), 148 (57), 122 (60), 108 (100), 69 (95), 43 (85), 41 (90); CIMS (pos.) *m/z* 459 $[M+H]^+$; CIMS (neg.) *m/z* 457 $[M-H]^-$; ^1H NMR ($CDCl_3$): δ 10.18 (1H, *s*, H-1), 5.05 (1H, *t*, *J* = 7 Hz, H-22), 5.01 (1H, *t*, *J* = 7 Hz, H-14), 3.6 (2H, *t*, *J* = 6 Hz, H-3), 3.35

(1H, *dd*, $J = 9$ and 7.5 Hz, H-6), 2.65 (1H, *t*, $J = 6.3$ Hz, H-18), 2.63/2.15 (2H, *m*, H-8), 2.06/2.00 (2H, *m*, H-16), 2.04 (2H, *m*, H-21), 1.88 (1H, *m*, H-10), 1.79 (2H, *m*, H-13), 1.78 (3H, *s*, H-25), 1.66 (3H, *s*, H-24), 1.64 (2H, *m*, H-5), 1.61/1.37 (2H, *m*, H-9), 1.60/1.52 (2H, *m*, H-17), 1.60/1.38 (2H, *m*, H-20), 1.58 (3H, *s*, H-30), 1.51 (3H, *s*, H-28), 1.3 (2H, *m*, H-4), 1.21 (3H, *s*, H-29), 1.17/1.09 (2H, *m*, H-12), 0.96 (3H, *s*, H-26), 0.8 (3H, *d*, $J = 7$ Hz, H-27); ^{13}C NMR ($CDCl_3$): δ 189.9 (*d*, C-1), 163.3 (*s*, C-7), 134.3 (*s*, C-15), 133.3 (*s*, C-2), 131.8 (*s*, C-23), 124.9 (*d*, C-14), 123.7 (*d*, C-22), 63.4 (*d*, C-18), 62.9 (*t*, C-3), 60.8 (*s*, C-19), 31.5 (*t*, C-4), 24.0 (*t*, C-5), 43.3 (*d*, C-6), 40.1 (*s*, C-11), 38.8 (*t*, C-20), 36.3 (*t*, C-16), 35.7 (*d*, C-10), 31.7 (*t*, C-12), 30.5 (*t*, C-9), 27.4 (*t*, C-8), 27.2 (*t*, C-17), 25.7 (*q*, C-24), 24.2 (*q*, C-26), 23.8 (*t*, C-21) 21.1 (*t*, C-13), 17.7 (*q*, C-30), 16.5 (*q*, C-29), 15.9 (*q*, C-28), 15.2 (*q*, C-27), 10.8 (*q*, C-25).

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