

ISOLATION AND STRUCTURE DETERMINATION OF A NEW IRIDAL FROM *IRIS SIBIRICA*

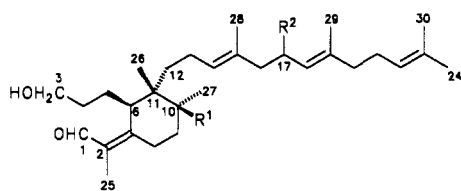
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ABSTRACT.—A new iridal, (6*R*,10*S*,11*S*)-17,29-didehydroiridal (**5**), has been isolated from a rhizome extract of *Iris sibirica*. Its structure was elucidated by spectroscopic methods. The compound is presumably derived from the 17,29-dehydrogenation of iridal (**1**).

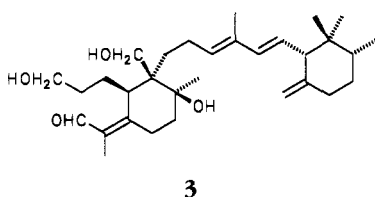
During previous investigations, we were able to isolate numerous iridals, representing a family of unusual monocyclic, bicyclic, and spirocyclic triterpenoids (e.g., structures **1–4**), from lipid-soluble extracts of sword lilies (1–3). For studies on the biosynthesis and metabolism of these compounds we periodically isolate preparatively useful amounts (100–200 mg) of 10-deoxy-17-hydroxyiridal

[2] from *Iris sibirica* L. (Iridaceae) rhizomes, which we use as a starting material for the synthesis of possible intermediates. Upon thorough analysis of the fractions obtained by mpls of the crude extract on RP-18, trace amounts of a new iridal were detected, which showed in its uv spectrum a λ max of 234 nm, so far observed only for the C₃₁ cycloiridals (4), thus suggesting the presence of a conjugated diene moiety in the molecule. The compound was isolated by semi-prep. hplc on RP-18. The eims of **5** revealed a molecular ion at m/z 456 and prominent fragment ions at m/z 135 and 69. In conjunction with its ¹³C-nmr data, a molecular composition of C₃₀H₄₈O₃ was determined for **5**. Comparison of the ¹H- and ¹³C-nmr data (Table 1) of **5** with previous results showed the presence of the seco-ring A system typical for all iridals (3). Therefore, the conjugated diene had to be located in the homofarnesyl side-chain. ¹H-nmr, ¹H,¹H-COSY, and ¹H decoupling experiments showed that a bisallylic CH₂ at δ 2.7 was solely coupled to an olefinic proton at δ 5.76, which in turn was connected to a second olefinic methine at δ 6.15. A coupling constant of 16 Hz indicated the *E* configuration of the double bond. The signal at δ 6.15 showed allylic coupling to a signal at δ 5.00, which was derived from one proton of an olefinic CH₂ group, the other appearing at δ 4.95. Therefore, a =C(R)-CH₂-CH=CH-C(R)=CH₂ grouping had to be present. This moiety is located in the center of the homofarnesyl chain, since a bisallylic CH₂ group cannot be positioned at C-12 and because an ole-

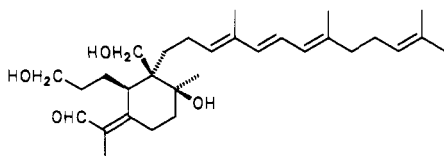


1 R¹=OH, R²=H

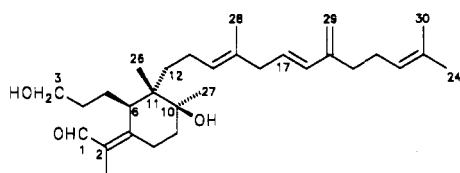
2 R¹=H, R²=OH



3



4



5

TABLE 1. ^{13}C - (100.6 MHz) and ^1H - (400 MHz) Nmr Data of **5**.^a

Position	^{13}C Nmr ^b	^1H Nmr ^c
1	190.1	10.41 (s)
2	132.0	
3	63.6	3.29 (t, 6)
6	44.0	3.21 (br d, 12)
7	162.4	
10	75.1	
11	45.5	
14	125.5	5.16 (br t, 7)
15	135.1	
16	44.1	2.72 (d, 7)
17	127.2	5.76 (dt, 16, 7)
18	134.8	6.15 (br d, 16)
19	146.9	
22	126.2	5.21 (br t, 7)
23	133.9	
24	26.5	1.66 (br s)
25	11.8	1.89 (s)
26	18.6	0.91 (s)
27	26.7	0.77 (s)
28	16.9	1.65 (br s)
29	114.8	5.00 (br s), 4.95 (br s)
30	18.4	1.54 (br s)

^aRun in C_6H_6-d_6 . Assignments are based on ^1H , ^1H - and ^1H , ^{13}C -COSY experiments and comparison with data of other iridals (3).

^bIn addition, signals for CH_2 groups at δ 38.2, 37.8, 33.6, 33.4, 28.0, 27.7, 24.5, and 23.4 were not assigned.

^cChemical shifts δ (ppm) relative to TMS. Signal multiplicity and coupling constants (Hz) are in parentheses.

finic proton at δ 5.21 showed allylic coupling to two methyl groups (δ 1.66 and 1.54), proving that the terpenoid chain is terminated by a common isoprene unit. Additional confirmation was given by the eims fragment ions at m/z 69 and 135, which are derived from cleavage of the side-chain between C-20/C-21 and C-16/C-17, respectively. Thus, from these spectral data, compound **5** was identified as 17,29-didehydroiridal. From biosynthetic considerations and from the identical nmr data of the ring system, we have assigned to **5** the same (6*R*,10*S*,11*S*)-configuration as found for all iridals (**5**). This is the first example of a monocyclic iridodiene. As pointed out earlier (6), the more common iridotrienes (e.g., **4**) develop by dehydrogenation of iridal [**1**] at

C-16/C-17. Presumably the dehydrogenase responsible for this reaction abstracts hydrogen from C-17 and C-29 to a minor extent, thus forming compound **5**.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Analytical hplc: Kontron model 200; column, LiChroCart RP-18 (125 mm, 4 mm i.d., Merck); solvent, $\text{MeOH-H}_2\text{O}$, 7:3 (5 min), linear gradient to 100% MeOH (15 min), 100% MeOH (20 min); flow rate 1 ml/min; detection, Hewlett-Packard-1040A diode-array detector. Uv spectra were recorded during each hplc analysis. Prep. hplc: Altex model 420; column, Spherisorb 5 ODS (240 mm, 5 mm i.d.). Mplc: Büchi model 681; column, RP-18 14–40 μm (240 mm, 20 mm i.d.). Nmr spectra: Bruker AM-400 (^1H : 400 MHz, ^{13}C : 100.6 MHz) in C_6H_6-d_6 . Eims: Finnigan-MAT 4510 gc-ms (70 eV).

PLANT MATERIAL.—Rhizomes of *I. sibirica* were purchased from Bornträger & Schlemmer, D-67591 Offstein, Germany, in April 1992.

EXTRACTION AND ISOLATION.—Extraction of the rhizomes was performed as previously described (7) to yield 2.5% of the essential oil. The crude extract (4 g) was separated by mplc using a $\text{MeOH-H}_2\text{O}$ (70:30) to MeOH gradient. The fractions eluting with $\text{MeOH-H}_2\text{O}$ (75:25) contained *inter alia* compound **5**, which was purified by prep. hplc ($\text{MeOH-H}_2\text{O}$, 80:20) to give 9.8 mg (0.25%) of a glassy solid, which proved to be very labile, rapidly decomposing in different solvents or in the dry state. Because it is stable for some time in C_6H_6 solution, the nmr spectra were recorded using this solvent.

(6*R*,10*S*,11*S*)-17,29-Didehydroiridal [**5**].—Uv λ max (MeOH) 234, 255 (sh) nm; eims m/z 456 [$\text{M}]^+$ (3), 438 (1), 387 (1.5), 369 (1), 135 (100), 109 (50), 93 (53), 69 (67), 43 (55); ^1H - and ^{13}C -nmr data, see Table 1.

ACKNOWLEDGMENTS

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