$[\alpha]^{27}_D$ –61° (c 0.5, $CHCl_3$) [lit.[39] mp 158–159 °C; $[\alpha]^{25}_D$ –67.8° (c 0.5, $CHCl_3$)].

17β-(Salicylideneamino)-5-androsten-3β-ol was sublimed at 160 °C (0.02 mm); mp 224–226 °C.

Anal. Calcd for $C_{26}H_{35}NO_2$: C, 79.34; H, 8.96. Found: C, 79.09; H, 8.95.

Registry No. (*S*)-**3b** *N*-salicylidene, 81477-47-6; (*S*)-**3c** *N*-salicylidene, 81477-48-7; **13a**, 5865-17-8; **13a** *N*-salicylidene, 21934-19-0; **13b**, 5865-18-9; **13b** *N*-salicylidene, 81520-64-1; **15a**, 2206-20-4; **15a** *N*-acetyl, 40937-16-4; **15a** *N*-salicylidene, 81477-49-8; **17a**, 2206-21-5; **17a** *N*-acetyl, 1912-64-7; **17a** *N*-salicylidene, 81496-95-9; **17b** *N*-salicylidene, 81477-50-1; **20a**, 7738-80-9; **20a** *N*-salicylidene, 21934-24-7; **21**, 4350-66-7; **21** *N*-salicylidene, 81477-51-2; **22** *N*-salicylidene, 81505-43-3; 11-oximino-5β-pregnane-3α,20β-diol, 5865-16-7; salicylaldehyde, 90-02-8; 3α-azido-5α-cholestane, 15067-20-6; 3-oximino-5α-cholestane, 2735-21-9; 3β-hydroxy-5α-androstan-17-one, 481-29-8.

Irigermanal and Iridogermanal: Two New Triterpenoids from Rhizomes of *Iris germanica* L.

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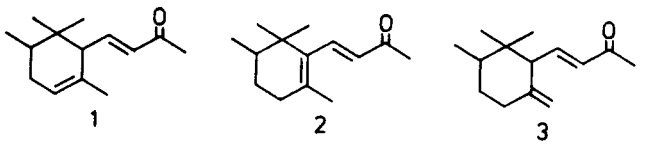
α-Irigermanal (**8a**), γ-irigermanal (**8b**), and iridogermanal (**12**) are the major extractable lipids of the rhizomes of *Iris germanica*, constituting about 1% of their fresh weight. The structure of the compounds was determined by detailed spectral analysis, chemical degradation, and X-ray crystallography. **8b** crystallizes as a methanol solvate in the space group $P2_1$ with a = 13.05 (1) Å, b = 8.84 (2) Å, c = 13.78 (1) Å, β = 105.84 (5)°, and Z = 2. The irigermanals are the first known bicyclic triterpenoids, and iridogermanal is the first monocyclic triterpenoid found so far. The compounds are closely related to ambreine.

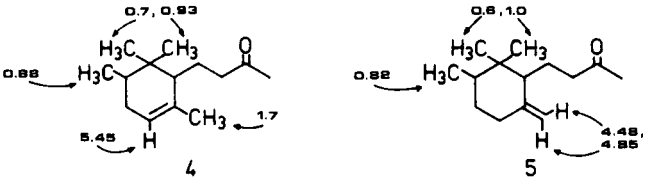
The sword-lily *Iris* has been cultivated since ancient times, and its rhizomes have been collected because they were known to contain, increasingly on storage, aromatic principles that were used to prepare perfumes and cosmetics with the fragrance of sweet violet.[1] It took some 50 years since the turn of the century and many controversies to determine the structures of the scent-carrying compounds as the three isomeric irones of 6-methylionones (**1** = α-irone, **2** = β-irone, **3** = γ-irone).[2] Just 10 years ago Rautenstrauch and Ohloff[3] published their final studies on the stereochemistry of these ketones.



1 **2** **3**

Our interest in the biosynthesis of the methylionones and the well-known fact that the irones do not occur in freshly harvested rhizomes, which have to be stored for years to contain the maximal amount,[4] led us to postulate that there have to be precursors that yield the ketones, possibly by oxidative degradation on storage.

Lipid extracts of the rhizomes of *Iris florentina* and *Iris pallida* right after their harvest do not contain irones. On treatment with various oxidizing agents ((pyridine)-chlorochromate, permanganate), however, violet-like scent is evolved, and it is possible to show the formation of irones by gas chromatography. On the other hand, the main oxidation product of such extracts from fresh *Iris germanica* rhizomes are two other compounds of slightly less polar behavior than the irones. Mass spectrometry gave a molecular ion at m/e 208. Comparison of the spectral properties and the gas chromatographic behavior with synthetic samples proved them to be α-dihydroirone (**4**)



and its γ-isomer (**5**). The presence of the corresponding precursors seems to depend on the season. We found **4** to be the major oxidation product in extracts from *I. germanica* rhizomes harvested in autumn, whereas **5** is mainly found in spring.

Isolation. To isolate the precursors of **4** and **5** the chopped rhizomes were extracted with methanol and chloroform; the combined extracts were concentrated to a viscous yellow oil. Silica gel and reversed-phase chromatography resulted in the isolation of glasslike iridogermanal and α- or γ-irigermanal, respectively.

Structure Determination. The mass spectra of α- and γ-irigermanal were almost identical. The molecular ion is m/e 472 and fragment ions are 457, 454, 439, 436, and 421 for loss of methyl groups and water. High-resolution mass measurements gave elemental compositions of $C_{31}H_{52}O_3$ for the molecular ions. The IR spectra and the loss of two molecules of water from the molecular ion implied the presence of two hydroxy groups. The third oxygen had to be an α,β-unsaturated aldehyde as shown by IR, NMR,

(1) Tschirch, A., "Handbuch der Pharmakognosie", C. H. Tauchnitz, Verlag, Leipzig, Germany, 1917.
(2) (a) Naves, Y. R., Grampoloff, A. V., and Bachmann, P., *Helv. Chim. Acta*, **30**, 1599 (1947); (b) Ruzicka, L., Schinz, H., Seidel, C. F., and Tavel, C., *ibid*, **30**, 1810 (1947).
(3) Rautenstrauch, V. and Ohloff, G., *Helv. Chim. Acta*, **54**, 1776 (1971).
(4) Crabalona, J., *Fr. Ses Parfums*, **13**, 22 (1959).

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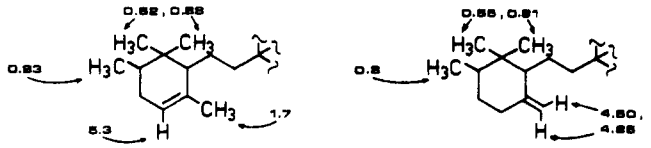
Table I. Tabulated ^{13}C NMR Data for *Iris germanica* Metabolites, Irones, and Dihydroirones

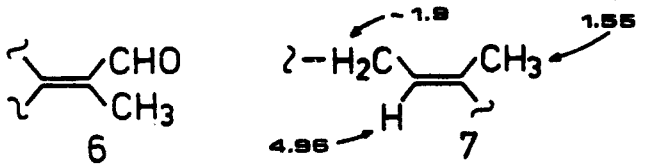
	compound[f]						
C no.	1[a]	4[a]	8a[b,e]	3[a]	5[a]	8b[a,e]	12[b,e]
1			190.1			190.1	190.1
2			133.2			132.8	133.2
3			63.0			62.5	63.0
6			43.6			43.3	43.6
7			162.8			163.6	162.8
10			75.0			74.9	75.0
11			44.9			44.6	44.9
14			124.2			123.6	124.2
15	198.1	208.7	136.1	198.2	209.6	135.9	135.2
16	131.8	45.6		133.6	43.1		
17	149.4	23.0		147.1	19.0		
18	55.9	50.3	50.5	57.8	53.4	52.9	127.8[c]
19	134.1	135.3	136.5	148.8	148.6	148.7	131.7
20	122.9	122.6	121.7	36.2[c]	37.7[c]		48.2
21	31.7	31.8		31.8[c]	33.4[c]		65.9
22	37.7	38.6	38.7	41.9	42.3	42.2	128.3[c]
23	35.6	36.1	36.1	38.7	39.5	39.0	134.6
24	15.2[d]	15.8[d]	16.0[d]	15.8[d]	16.4[d]	15.8[d]	25.7[d]
25			10.9			10.8	10.9
26			26.3			25.9	26.3
27			17.9			17.8	17.9
28	26.8	29.9	16.1	27.2	30.0	16.3	16.2
29	22.8	22.5	22.6	108.7	106.5	106.2	15.8
30	14.4[d]	14.3[d]	14.6[d]	14.3[d]	14.0[d]	14.0[d]	18.2[d]
31	26.4	26.3	26.4	27.6	26.6	26.5	

[a] Spectra recorded in $CDCl_3$ at 90 MHz. [b] Recorded in $CDCl_3$ at 400 MHz. [c,d] Assignments may be reversed. [e] Methylene carbons are not assigned: (8a) 42.3, 37.4, 37.1, 32.8, 32.1, 27.1, 26.8, 23.9, 22.3; (8b) 38.4, 37.6, 37.2, 36.7, 33.3, 32.4, 26.5, 23.8, 23.1, 21.9; (12) 43.3, 39.5, 37.3, 37.1, 32.8, 26.8, 26.5, 22.2. [f] Refer to structures 8a, 13 for carbon numbers.[12]

and UV data. Comparison of the ^1H NMR and ^{13}C NMR resonances (for ^{13}C data see Table I) with the spectra of **4** and **5** clearly indicated that the α- or γ-dihydroirone moiety is part of the respective molecule. The connection to the other part of the molecule had to be in C(3) of the side chain. In addition to this portion some structural elements were identified by spin–spin decoupling and resolution-enhancement experiments on α-irigermanal at 400 MHz.

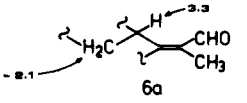


The aldehyde proton at δ 10.3 shows only a small coupling to the allylic methyl group at 1.84. Carbonyl and methyl groups therefore have to be attached to a carbon of a completely substituted double bond. The methylene protons at δ 3.6 are coupled to another CH_2 at 1.35, which indicated the presence of a CH_2CH_2OH moiety. One olefinic proton at 4.96 gave allylic coupling to a methylene at 1.9 and homoallylic to the methyl group at 1.55, which leads to partial structure **7**. The two methyl groups at

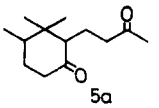


1.11 and 1.19 showed no coupling and therefore had to be connected to quarternary carbons.

Finally the ^{13}C NMR (Table I) showed, in addition to the methylene carbon at δ 63.0 for the primary alcohol function, a resonance for a quarternary carbon at δ 75.0, indicating the second hydroxy group to be tertiary. The resonance of one olefinic carbon appears at 162.8 and was attributed to the carbon in the β position to the aldehyde function. Presumably it had to be part of a ring system. The exocyclic nature of the double bond and the influence of the carbonyl group thus would explain the downfield shift of this resonance. The methine group, the proton of which appears as a dd at δ 3.3, must be attached to this carbon and couples with two nonequivalent protons of a methylene group around 2.1. This allowed expansion of the partial structure **6** to **6a**, which was confirmed by some reactions on α-irigermanal. Reduction of the carbonyl



group with $NaBH_4$/alumina[5] yielded the corresponding primary alcohol and resulted in a shift of the ^1H NMR resonance of this methine poton to δ 2.6. The same effect was observed when derivatives of the aldehyde (semicarbazone, 2,4-dinitrophenylhydrazone) were prepared. The spectral data gave no further evidence about the structure, and the whereabouts of the three methylene groups so far are not assigned. All attempts to prepare crystalline derivatives (acetate, *p*-nitrobenzoic ester, semicarbazone, or 2,4-dinitrophenylhydrazone) of α-irigermanal failed. Experiments to chemically degrade the compounds by ozonolysis (with oxidative or reductive workup) resulted in the formation of a whole spectrum of products that we were not able to separate or identify. The above mentioned oxidation reactions when performed with pure α- or γ-irigermanal did not lead to other defined products except **4** or **5** and the diketone **5a** when γ-iri-



(5) Santaniello, E., Ponti, F., and Manzochi, A., *Synthesis*, 891 (1978).

Table II. Selected Bond Lengths (Å) and Angles (Deg)[a]

Bond Lengths

O(1)-C(1)	1.25 (2)	C(7)-C(8)	1.50 (2)	C(16)-C(17)	1.51 (2)
O(2)-C(3)	1.42 (1)	C(8)-C(9)	1.53 (2)	C(17)-C(18)	1.54 (2)
O(3)-C(10)	1.45 (1)	C(9)-C(10)	1.52 (2)	C(18)-C(19)	1.53 (2)
C(1)-C(2)	1.43 (2)	C(10)-C(11)	1.57 (2)	C(19)-C(29)	1.31 (2)
C(2)-C(7)	1.37 (2)	C(11)-C(12)	1.55 (2)	C(19)-C(20)	1.52 (2)
C(2)-C(25)	1.52 (2)	C(12)-C(13)	1.56 (2)	C(20)-C(21)	1.52 (2)
C(3)-C(4)	1.52 (2)	C(13)-C(14)	1.49 (2)	C(21)-C(22)	1.51 (2)
C(4)-C(5)	1.52 (2)	C(14)-C(15)	1.30 (2)	C(22)-C(23)	1.59 (2)
C(5)-C(6)	1.56 (2)	C(15)-C(16)	1.48 (2)	C(23)-C(18)	1.58 (2)
C(6)-C(11)	1.57 (2)	C(15)-C(28)	1.54 (2)		

Bond Angles

C(1)-C(2)-C(7)	120 (1)	C(6)-C(11)-C(27)	111 (1)
C(1)-C(2)-C(25)	116 (1)	C(12)-C(11)-C(27)	109 (1)
C(7)-C(2)-C(25)	124 (1)	C(11)-C(12)-C(13)	118 (1)
C(5)-C(6)-C(7)	110 (1)	C(12)-C(13)-C(14)	111 (1)
C(5)-C(6)-C(11)	116 (1)	C(13)-C(14)-C(15)	131 (1)
C(7)-C(6)-C(11)	113 (1)	C(14)-C(15)-C(16)	123 (1)
C(2)-C(7)-C(6)	126 (1)	C(14)-C(15)-C(28)	123 (1)
C(2)-C(7)-C(8)	121 (1)	C(16)-C(15)-C(28)	115 (1)
C(6)-C(7)-C(8)	113 (1)	C(15)-C(16)-C(17)	116 (1)
O(3)-C(10)-C(9)	108 (1)	C(16)-C(17)-C(18)	112 (1)
O(3)-C(10)-C(11)	107 (1)	C(18)-C(23)-C(22)	107 (1)
O(3)-C(10)-C(26)	108 (1)	C(18)-C(23)-C(24)	107 (1)
C(9)-C(10)-C(11)	111 (1)	C(18)-C(23)-C(30)	111 (1)
C(9)-C(10)-C(26)	110 (1)	C(22)-C(23)-C(24)	107 (1)
C(6)-C(11)-C(10)	110 (1)	C(22)-C(23)-C(30)	114 (1)
C(6)-C(11)-C(12)	107 (1)	C(24)-C(23)-C(30)	111 (1)

[a] Estimated standard deviations in parentheses.

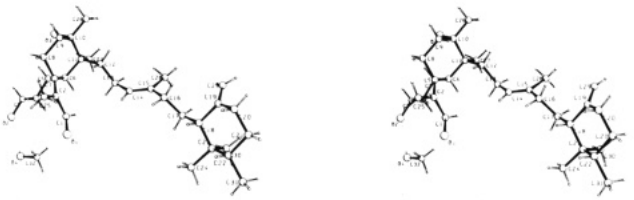
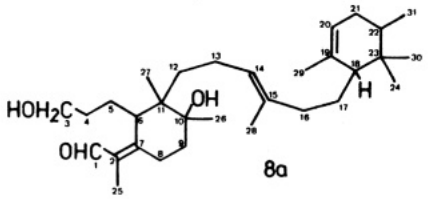
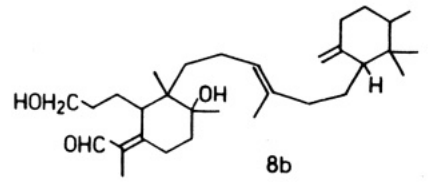


Figure 1. Stereoscopic view of **8b** with the atom numbering scheme used and the hydrogen-bonded methanol solvate molecule.

germanal is oxidized with permanganate. So it was impossible to assign a structure to the second half of the molecules. At this point we were able to crystallize γ-irigermanal from a saturated solution in methanol and to perform an X-ray crystal structure determination (see Experimental Section). Figure 1 shows a stereoscopic view of the γ-irigermanal **8b**. According to the numbering



8a



8b

scheme in Figure 1, the most important bond lengths and angles are listed in Table II.

The molecular structure of **8b** resembles a squalene, in which cyclization to two six-membered rings has taken place at the chain ends. Both cyclohexane rings display nearly perfect chair conformations: the torsion angles in the ring C(6)–C(11) are ±51–55° and in the ring C(18)–C(23) ±56–60°. The carbon chain C(12)–C(17), linking both six-membered rings, is axially bonded at C(11) and equatorially at C(18). According to the nomenclature used by Flory,[6] the chain conformation can be depicted symbolically as $T\bar{S}\,E\,ST$.[7] These symbols refer to the torsion angles between the chain carbon atoms from C(12) to C(17). In the crystal structure of squalene,[8] a number of cis (≙C) conformations have been observed, and ^{13}C NMR spectra in different solvents have shown no indications for other conformations in solution.[8,9] The rigid and bulky ring groups in **8b** impose a different molecular shape, because a C(14)–C(15)–C(16)–C(17) torsion angle near 0° (cis ≙C) would bring these groups too close together.

All bond distances and angles in **8b** are in the expected range, with exception of the cyclohexane bonds C(10)–C(6), C(10)–C(11), and C(23)–C(18), C(23)–C(22), which seem to be significantly stretched to 1.57–1.59 (2) Å by crowding with four nonhydrogen substituents at C(11) and C(22).

Crystals of **8b** are build up of helical chains along the 2-fold screw axis. The solvent, methanol, links the single molecules by two different hydrogen bonds: O(4)···O(2)′ (2.78 Å) and O(4)···O(2)″ (2.81 Å) with symmetry transformations $(-x, {}^1/_2 + y, -z)$ and $(x, 1 + y, z)$ on the $CH_2O(2)H$ groups. A further hydrogen bond from the hydroxy group O(3)–H to the aldehyde oxygen O(1)′ (symmetry transformation $x, 1 + y, z$; O(3)···O(1)′ 2.82 Å) completes the hydrogen bonding scheme, in which all possible hydrogen bonds are satisfied.

Structures **8a** and **8b** are in accordance with the spectroscopic results discussed above.

The third compound isolated from fall as well as from spring rhizomes of *I. germanica* was the somewhat more

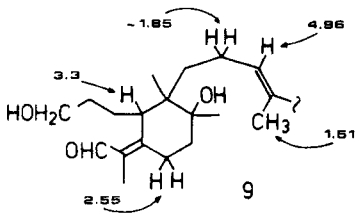
(6) Abe, Y. and Flory, P. J., *Macromolecules*, **4**, 230 (1971).

(7) The symbols *C*, *G*, *S*, and *T* are used for single-bond torsion angles of 0° (cis), 60° (gauche), 120° (skew), and 180° (trans); the symbols *E* and *Z* are used for the double bonds. $\bar{S}$ means a negative sign for the torsion angle.

(8) Ernst, J. and Fuhrhop, J.-H., *Justus Liebigs Ann. Chem.*, 1635 (1979).

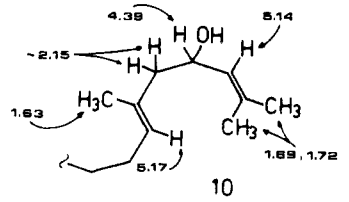
(9) van Dommelen, M. E., Wilson, A. R. N., de Haan, J. W., and Buck, M. M., *Rec. Trav. Chim. Pays-Bas*, **94**, 206 (1975).

polar iridogermanal. Its electron-impact (EI) mass spectrum did not show a molecular ion. Fragment ions appeared at m/e 456, 441, 438, 423, and 420 for loss of methyl groups and water, and high-resolution mass measurements gave an elemental composition of $C_{30}H_{48}O_3$ for the m/e 456 peak. A molecular ion, however, was easily seen at m/e 474 in the negative ion chemical ionization (NCI) mass spectrum. Thus the compound had the formula $C_{30}H_{50}O_4$, and m/e 456 in the EI spectrum accounted for the loss of one molecule of water. As with the irigermanals, IR and UV spectra only showed the presence of hydroxy and α,β-unsaturated carbonyl functions. From the ^1H NMR and the ^{13}C NMR spectra of iridogermanal it was easily deduced that the resonances for the multisubstituted six-membered ring are identical with the corresponding signals of the irigermanals. Thus the partial structure **9**

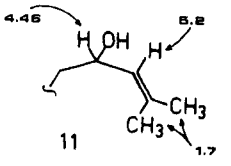


9

again had to be present. Since the compound contains an additional double bond as seen in the ^{13}C NMR there was no unsaturation left for a second ring system. Therefore the irone ring was not present, but this part of the molecule had to be open chained. Spin–spin decoupling and resolution enhancement experiments at 400 MHz revealed this part of the molecule as **10**. The values found are in ex-



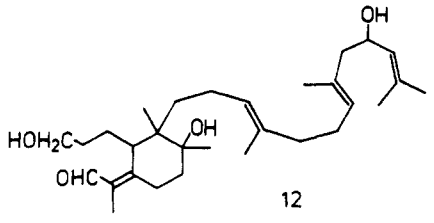
10



11

cellent agreement with the reported chemical shifts of xeniaphyllenol,[10] a part of which (**11**) has the same structure.

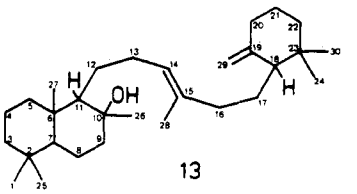
Confirmed was partial structure **10** by oxidation of iridogermanal with (pyridine)chlorochromate/alumina.[11] In the ^1H NMR spectrum of the resulting ketone the olefinic proton's resonance was shifted to δ 6.2, and the methylene group now appeared as a singlet at δ 3.0. The complete structural skeleton of iridogermanal thus can be written as **12**. It is noteworthy to mention that the three com-



12

pounds are found in less polar fractions as esters of fatty acids at C(3)[12] with lauric acid (11%), myristic acid (46%), palmitic acid (9%), or linoleic acid (23%), respectively, as the ^1H NMR signal of the methylene protons is shifted to δ 4.05. Apparently transesterification partly occurs during the extraction procedure. Crude extracts prepared by extraction with methanol contain appreciable amounts of methyl esters of the acids mentioned above, whereas in acetone extracts of the rhizomes no methyl esters are found. Moreover the free alcohols are present in considerably smaller amounts in the acetone extracts.

The three compounds show a close relationship to ambreine (**13**), constituent of the ambergris of the sperm



13

whale,[13] which on oxidative degradation gives dihydroionone.[14] Its skeleton easily can be deduced from all *trans*-squalene by simultaneous cyclization from both ends. For the formation of iridogermanal **12** only a methyl-shift from C(6) to C(11) has to occur (see for precedence the formation of cucurbitacin B[15]) and the annelated ring system as to be cleaved. The problem if cyclization of the open chain of **12** to form the irone ring system in **8a** and **8b** is initiated by a methylene addition or if the extra methyl group is introduced as a substituent later yet has to be answered.

Experimental Section

^1H NMR spectra were obtained on a Varian EM-390 spectrometer and ^{13}C NMR spectra on a Varian CFT 20 spectrometer. Chemical shifts are reported in δ relative to Me_4Si (δ 0). Electron-impact (EI) mass spectra were recorded on a Varian MAT CH 7 A and a Finnigan 3200 mass spectrometers at 100 and 70 eV, respectively. Negative ion chemical ionization (NCI) experiments were carried out on a Finnigan 4510 mass spectrometer using NH_3 as reactant gas. IR spectra were determined on a Perkin-Elmer 457 and UV spectra on a Varian Cary 14 spectrometer. Optical rotations were measured on a Zeiss 0.005° precision polarimeter. For the high-performance liquid chromatography an Altex 420 HPLC system equipped with a Kontron 720LC UV monitor was used. The solvent for preparative low-pressure liquid chromatography was delivered (3–5 mL/min) by a Beckman AccuFlow pump equipped with a second pump head. Gas chromatographic separations were carried out on a Carlo Erba 2900 capillary column GC equipped with WCOT columns (50 m, 0.4 mm i.d.) coated with OV 101 and Ucon 75 H 90000, respectively.

Isolation. Rhizomes of *Iris germanica* harvested in spring or autumn were obtained by Bornträger & Schlemmer, D-6521 Offstein, West Germany.

The rhizomes (1 kg) were cleaned, cut into pieces, with addition of a little water mashed in a Waring blender and extracted twice with 250 mL of methanol and twice with 250 mL of chloroform. A mixture of 500 mL of methanol/water (1:1) was added to the combined extracts and the resulting solution was extracted six times with 150 mL of ether. The ethereal solution was dried over $MgSO_4$ and evaporated to give 25 g of a viscous yellow oil.

The crude extract was applied to a 2.5 × 100 cm column of silica gel and chromatographed with a petroleum ether/chloroform/acetone/methanol gradient. The fraction eluted with 70% $CHCl_3$/30% acetone (5.2 g) consisted of fatty acid esters of **12** and **8a** or **8b**. The crude irigermanals **8a** or **8b** were eluted with 100% acetone, whereas the more polar iridogermanal **12** was obtained with 90% acetone/10% methanol. Each compound was subsequently purified by low-pressure liquid chromatography on a Merck Lobar Lichroprep RP 8-column by using methanol/water (80:20 or 90:10) as the eluent.

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Fatty Acid Esters. Due to the small differences in polarity, the esters of **8a** or **8b** and **12** were not completely separated. ^1H NMR analysis proved the nature of the mixture since all signals of the irigermanals or iridogermanals were present with only the resonance of the methylene protons at δ 3.6 shifted to δ 4.05. Fatty acid composition was determined by transesterification of the mixture with methanol/HCl followed by gas chromatographic analysis (column: 2 m 10% SP 2330 on 100/120 Chromosorb W AW by Supelco Inc.). The following acids were found (%): $C_{10:0}$ (2); $C_{12:0}$ (11); $C_{14:0}$ (46); $C_{16:0}$ (9); $C_{18:1}$ (6); $C_{18:2}$ (23); $C_{18:3}$ or $C_{20:0}$ (3), and trace amounts of $C_{14:1}$, $C_{16:1}$, and $C_{18:0}$.

α-Irigermanal (8a) (2.45 g) formed a glasslike solid. All attempts to crystallize the compound failed; $[\alpha]^{20}_D$ + 36° (CH_2Cl_2, *c* 7.2); IR (KBr) ν_{max} 3430, 2980, 2940, 2895, 1685, 1640, 910 cm^{-1}; UV (EtOH) λ_{max} 256 nm (ϵ 14 100); EI mass spectrum, *m/e* 472 (M^+), 457, 454, 439, 436, 421, 414, 395, 371; high-resolution mass measurement, *m/e* 472.392 465 0 ($C_{31}H_{52}O_3$ requires 472.391 624 0); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.62 (s, 3 H), 0.83 (d, *J* = 6 Hz, 3 H), 0.88 (s, 3 H), 1.11 (s, 3 H), 1.19 (s, 3 H), 1.55 (d, *J* = 1.2 Hz, 3 H), 1.7 (m, *J* = 1.2 Hz, 3 H), 1.84 (d, *J* = 1.2 Hz, 3 H), 1.0–2.2 (m, 20 H), 2.55 (m, 2 H), 3.3 (dd, *J* = 10.3 Hz, *J* = 1.5 Hz, 1 H), 3.6 (t, *J* = 6.2 Hz, 2 H), 4.96 (t quart, *J* = 6.7 Hz, *J* = 1.2 Hz, 1 H), 5.3 (m, 1 H), 10.3 (d, *J* = 1.2 Hz, 1 H).

γ-Irigermanal (8b) (2.04 g) crystallized from a saturated solution in methanol as white needles: mp 74–75 °C; $[\alpha]^{20}_D$ + 10° (CH_2Cl_2, *c* 14.4); IR (KBr) ν_{max} 3420, 3090, 2985, 2900, 2875, 1690, 1630, 890 cm^{-1}; UV (EtOH) λ_{max} 256 nm (ϵ 14 100); EI mass spectrum, *m/e* 472 (M^+), 457, 454, 439, 436, 421, 395; high-resolution mass measurement, *m/e* 472.391 073 1 ($C_{31}H_{52}O_3$ requires 472.391 624 0); ^1H NMR ($CDCl_3$, 90 MHz) δ 0.55 (s, 3 H), 0.8 (d, *J* = 6 Hz, 3 H), 0.91 (s, 3 H), 1.05 (s, 3 H), 1.12 (s, 3 H), 1.5 (br s, 3 H), 1.82 (br s, 3 H), 1.0–2.2 (22 H), 2.5 (m, 2 H), 3.3 (dd, *J* = 10 Hz, 1.5 Hz, 1 H), 3.55 (t, *J* = 6 Hz, 2 H), 4.5 (br s, 1 H), 4.85 (br s, 1 H), 4.96 (t, *J* = 6 Hz, 1 H), 10.3 (br s, 1 H).

Anal. Calcd for $C_{31}H_{52}O_3$: C, 78.76; H, 11.09. Found: C, 78.60; H, 10.93.

Iridogermanal (12) (2.73 g) was isolated as a glasslike solid which did not crystallize. $[\alpha]^{20}_D$ + 41° (CH_2Cl_2, *c* 15.3); IR (KBr) ν_{max} 3430, 2995, 2960, 2900, 1695, 1650, 920 cm^{-1}; UV (EtOH) λ_{max} 256 nm (ϵ 13 000); EI mass spectrum, *m/e* 456 ($M - H_2O)^+$, 441, 438, 423, 420, 390, 372; high-resolution mass measurement, *m/e* 456.360 326 0 ($C_{30}H_{48}O_3$ requires 456.359 642 4); NCI mass spectrum (NH_3), *m/e* 474 (M^-); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.08 (s, 3 H), 1.16 (s, 3 H), 1.51 (d, *J* = 1.2 Hz, 3 H), 1.63 (d, *J* = 1.2 Hz, 3 H), 1.69 (d, *J* = 1.2 Hz, 3 H), 1.72 (d, *J* = 1.2 Hz, 3 H), 1.83 (d, *J* = 1.2 Hz, 3 H), 1.1–1.7 and 1.7–2.2 (19 H), 2.55 (m, 2 H), 3.3 (dd, *J* = 10.4 Hz, 1.5 Hz, 1 H), 3.6 (t, *J* = 6.4 Hz, 2 H), 4.39 (dt, *J* = 8.4 Hz, 4.3 Hz, 1 H), 4.96 (t quart, *J* = 7.6 Hz, 1.2 Hz, 1 H), 5.14 (d quint, *J* = 8.4 Hz, 1.2 Hz, 1 H), 5.17 (t quart, *J* = 7.6 Hz, 1.2 Hz, 1 H), 10.3 (d, *J* = 1.2 Hz, 1 H).

Oxidations. A. With (Pyridine)chlorochromate. A 10-mg sample of **8a** or **8b** was dissolved in 3 mL of methylene chloride and 0.5 g of (pyridine)chlorochromate[16] was added. The mixture was stirred at room temperature for 30 min, ether (10 mL) was added to precipitate the inorganic salts, and after filtration the solvent was removed in vacuo. The residue contained 0.1 mg (2%) of dihydroirone **4** or **5** as established by gas chromatography. No other defined products were found.

B. With $KMnO_4$. Following the procedure of Lederer et al.[14] 100 mg of **8a** or **8b** were dissolved in acetone (5 mL). The solution was refluxed, and 330 mg of $KMnO_4$ was added in portions within 30 min. Refluxing was continued for 25 h, and after evaporation of the solvent the residue was eluted with ether (50 mL). Filtration and evaporation of the ether yielded in case of **8a**-25 mg of crude **4**, which was purified by low-pressure LC to give 10.5 mg of pure α-dihydroirone (**4**). In case of **8b** 30.3 mg of product was formed, consisting of **5** and **5a** in a 1:1 ratio. Separation of the γ-dihydroirone (**5**) and the diketone (**5a**) was achieved by low-pressure LC on RP 8 to yield 5.5 mg of **5** and 5.3 mg of **5a**.

α-Dihydroirone (4): EI mass spectrum, *m/e* (rel intensity) 208 (10, M^+), 190 (6), 175 (3), 150 (69), 135 (100), 121 (32), 107 (39), 95 (91), 79 (21), 67 (14), 55 (13), 43 (32); ^1H NMR ($CDCl_3$, 90 MHz) δ 0.75 (s, 3 H), 0.88 (d, *J* = 6 Hz, 3 H), 0.93 (s, 3 H), 1.1–2.7 (8 H), 1.7 (br s, 3 H), 2.15 (s, 3 H), 5.45 (br s, 1 H); Kováts indices[17] OV 101 (180 °C) 1552.3 ± 2.3, Ucon 75 H 90 000 (180 °C) 1899.4 ± 0.6.

γ-Dihydroirone (5): EI mass spectrum, *m/e* (rel intensity) 208 (8, M^+), 193 (6), 190 (16), 175 (43), 150 (70), 135 (84), 123 (42), 107 (100), 83 (53), 55 (28), 43 (43); ^1H NMR ($CDCl_3$, 90 MHz) δ 0.6 (s, 3 H), 0.82 (d, *J* = 6 Hz, 3 H), 1.0 (s, 3 H), 1.0–2.7 (10 H), 2.15 (s, 3 H), 4.48 (s, 1 H), 4.85 (s, 1 H); Kováts indices OV 101 (180 °C) 1523.4 ± 0.1, Ucon 75 H 90 000 (180 °C) 1853.7 ± 0.8.

3-Oxodihydroirone (5a): EI mass spectrum, *m/e* (rel intensity) 210 (3, M^+), 195 (46), 177 (9), 153 (13), 125 (42), 83 (55), 54 (49), 41 (100); ^1H NMR ($CDCl_3$, 90 MHz) δ 0.55 (s, 3 H), 0.91 (d, *J* = 6 Hz, 3 H), 1.1 (s, 3 H), 1.2–2.9 (10 H), 2.15 (s, 3 H); Kováts indices OV 101 (180 °C) 1593.2 ± 0.1, Ucon 75 H 90 000 (180 °C) 2131.0 ± 0.4.

C. With (Pyridine)chlorochromate/Alumina. A 40-mg iridogermanal (**12**) sample was dissolved in benzene (10 mL), and 1 g of (pyridine)chlorochromate/alumina[11] was added. Stirring at room temperature for 30 min, filtration, and evaporation of the solvent gave 24 mg of crude product, which was purified by low-pressure LC on RP 8 to yield 12 mg of a light yellow solid: EI mass spectrum, (rel intensity) *m/e* 470 (0.1 M^+), 83 (100); ^1H NMR ($CDCl_3$, 90 MHz) δ 3.0 (s, 3 H), 4.9 (t, 1 H), 5.2 (m, 1 H), 6.1 (s, 1 H), 9.8 (t, 1 H), 10.3 (br s, 1 H).

Reduction with $NaBH_4$/Alumina. To a suspension of 0.2 g of $NaBH_4$/alumina[5] in 3 mL of ether a solution of 30 mg of **8a** in ether (3 mL) was added. After being stirred at room temperature for 5 min, the solution was filtrated, and the residue washed three times with 5 mL of ether. The combined filtrates were dried over anhydrous $MgSO_4$, and the solvent was evaporated to yield 18 mg of product which was analyzed without further purification; EI mass spectrum (rel intensity) *m/e* 474 (1, M^+), 456 (17), 438 (8), 423 (3); ^1H NMR ($CDCl_3$, 90 MHz) δ 2.6 (dd, 1 H), 3.6 (t, 2 H), 4.25 (br s, 2 H), 5.05 (t, 1 H), 5.35 (m, 1 H).

Synthesis of α- (4) and γ-Dihydroirone (5). Following the procedure of Ojiwa and Kogure[18] 0.75 g of natural *Iris* oil (essence *Iris Absolue*, obtained by P. Kaders, Hamburg, West Germany) consisting of 60% α-irone (**1**) and 40% of the γ-isomer (**3**) was admixed to 12 mg of tris(triphenylphosphine)chlororhodium(I)[19] and 1.5 mL (80.0 mmol) of triethylsilane and heated to 50–60 °C. The reaction was observed by gas chromatography, and additional 0.5 mL of triethylsilane was added after 3, 6, and 17 h to ensure complete reaction. After 26 h all the irone had reacted to form the silylenol ether. For hydrolysis 15 mL of a mixture of methanol, acetone, and saturated K_2CO_3 solution (1:1:1) was added, and the mixture was kept at 50–60 °C for 3.5 h. After addition of water (20 mL) the mixture was extracted with ether (50 mL), and the ethereal layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The crude product was purified by chromatography on silica gel (50 g) with pentane/ether (90:10) as eluent to yield 268 mg (36%) of α- (**4**) and γ-dihydroirone (**5**). Separation of the two isomers was achieved by preparative GLC (column: 2.5 m × 4 mm i.d., 20% PEG 4M on Chromosorb P, 60–80 mesh, 175 °C). The spectroscopic properties of the synthetic dihydroirones were identical with those reported above for the oxidation products of **8a** and **8b**. The two synthetic isomers had the following Kováts indices: α-dihydroirone (**4**), OV 101 (180 °C) 1552.8 ± 0.6, Ucon 75 H 90 000 (180 °C) 1899.6 ± 0.9; γ-dihydroirone (**5**), OV 101 (180 °C) 1523.6 ± 0.1, Ucon 75 H 90 000 (180 °C) 1853.4 ± 0.2.

Crystal Structure Determination. Compound **8b** crystallized from methanol as clear, colorless needles, which became cloudy on exposure to air. In order to prevent loss of solvent and to enhance the poor diffraction quality, a fresh and clear crystal of approximate dimensions 0.10 × 0.25 × 0.8 mm^3 was mounted on an Enraf-Nonius CAD 4 diffractometer, which was linked with a cooling device (−100 °C, N_2). Accurate unit cell parameters and crystal orientation were determined by least-squares analysis of the setting angles for 25 reflections with $10° < \theta < 15°$, automatically centered on the diffractometer (Mo Kα, graphite monochromator). The values obtained are **a** = 13.05 (1) Å, **b** = 8.84 (2) Å, **c** = 13.78 (1) Å, β = 105.84 (5)°, and **V** = 1529.9 $Å^3$.

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Monoclinic diffraction symmetry was confirmed by a fast, low-angle data collection. The systematic absences $0k0$ ($k = 2n + 1$) indicated the space groups $P2_1$ and $P2_1/m$, the former of which proved to be correct by successful structure solution and refinement. Intensity data were recorded with ω/θ scans (variable scan speed, maximum measuring time 30 s) up to a 2θ range of 50°. After correction for Lorentz and polarization effects, a unique data set of 1842 reflections (with intensities greater than twice the background) was used for all further calculations.

After several attempts of routine application of direct methods had failed (MULTAN 80), a suitable starting set (chosen by hand) of 12 reflections could be expanded by weighted tangent refinement to 174 phase sets, one of which showed in an E map 30 atoms in sensible positions. The remaining atoms were located on an difference map, including the atoms of the solvent methanol. Full-matrix least-squares refinement with isotropic temperature factors led to $R = 0.15$. A difference Fourier synthesis, in which all reflections with $\sin\theta/\lambda \leq 0.3$ were doubly weighted, allowed the location of all hydrogen atoms. The H atoms linked to the C atoms were refined in idealized positions (C–H 0.96 Å) riding on the parent carbon atoms. The refinement converged at $R = 0.114$ and $R_G = 0.111$ ($R_G = [\sum\Delta^2/\sum wF_o^2]^{1/2}$). At this stage, we decided to stop the refinement process, because further refinement with anisotropic temperature factors seemed not to improve the observed molecular geometry. An analysis of variance was very flat with respect to $\sin\theta$ and F_{max}/F. This demonstrated that unit weights in least-squares refinement have been most suitable in this case. A final difference map was featureless. The final atomic parameters are given in Table III.

All calculations were carried out on Univac 1100/80 and Telefunken TR440 computers by using the programs SHELX (G. M. Sheldrick), XANADU (J. Roberts and G. M. Sheldrick), and the plot program PLUTO (S. Motherwell).

Acknowledgment. Thanks are due to B. Hanisch for her diligent help with numerous fractionations and to the Fonds der Chemischen Industrie for financial support. The recording of the 400-MHz spectra by Dr. H. Günther and P. Schmidt, Gesamthochschule Siegen, West Germany, is gratefully acknowledged.

Registry No. 1, 79-69-6; 3, 79-68-5; 4, 81456-93-1; 5, 81456-94-2; 5a, 81456-95-3; 8a, 81456-96-4; 8b, 81456-97-5; 12, 81456-98-6.

Supplementary Material Available: Listing of the fractional atomic coordinates (Table III) (1 page). Ordering information is given on any current masthead page.

Synthesis and Photochemistry of Steroidal β,γ-Unsaturated Ketones: An Approach to Reversible Steroid–Diterpenoid Interconversions[1]

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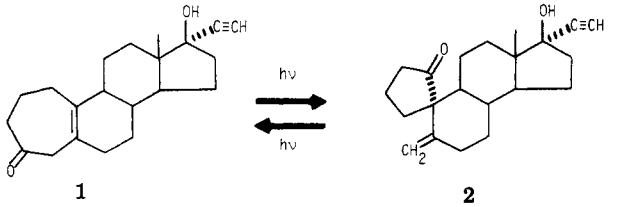
4,4-Dimethylandrost-8(14)-en-16-one (**3**) was synthesized in 14 steps from testosterone. Photolysis of **3** afforded the double-bond migration product 4,4-dimethyl-14β-androst-7-en-16-one (**8b**) together with a solvent-added product. Photolysis of the β,γ-unsaturated ketones **9**, **11**, and 4,4-dimethylandrost-8(14)-en-17-one (**16b**) afforded the [1,3] acyl shift products **10**, **12**, and 4,4-dimethyl-8α,17-cyclo-13,17-seco-5α-androst-13-en-17-one (**17**), respectively. Irradiation of **11** also afforded the photodecarbonylation products **13** and **14**, and **16b** gave the C-13 epimer **16a**. The α,α,α′,α′-tetramethyl β,γ-unsaturated ketone **15** was remarkably stable to photolysis.

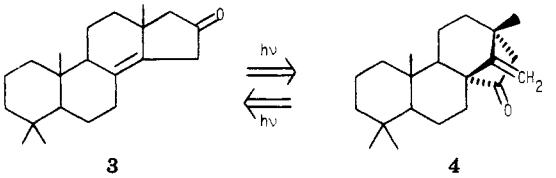
Due to the structural similarities between steroids and diterpenoids, there have been a number of studies involving the conversion of steroids into diterpenoids[2] and of diterpenoids into steroids.[3] We were interested in developing a reaction whereby steroids and diterpenoids could be interconverted reversibly. To this end the [1,3] acyl shift photoisomerization reaction of cyclic β,γ-unsaturated ketones appeared attractive.[4] Recently we have shown that the steroidal β,γ-unsaturated ketone **1** may be



1 **2**

photoisomerized to a photoequilibrium of **1** and **2**.[5] These isomers were easily separated and could be recycled to afford the desired isomer. Furthermore, this photoequilibrium was wavelength dependent, and by varying the wavelength of the exciting light the photoequilibrium may be shifted in the desired direction.[5]

Applying this photoisomerization reaction to the case in question suggests that the β,γ-unsaturated steroidal ketone **3** should afford the new β,γ-unsaturated di-



3 **4**

terpenoid[6] ketone **4**, via a [1,3] acyl shift. Furthermore, **4** should photoisomerize back to **3**. This latter reaction is important since several recent syntheses of tetracyclic diterpenoids[7] provide a convenient route for the synthesis of **4**. As an extension of this work, the photoepimerization of the C-18 methyl group in 17-keto steroids[8] should open

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