

Five New Peltogynoids from Underground Parts of *Iris bungei*: A Mongolian Medicinal Plant

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Five new peltogynoids, irisoids A—E (1—5), have been isolated from the underground parts of *Iris bungei*. The structures of the new compounds were established on the basis of spectroscopic methods and were found to be 1,8,10-trihydroxy-9-methoxy-[1]benzopyrano-[3,2-c][2]-benzopyran-7(5H)-one (1), 1,8-dihydroxy-9,10-dimethoxy-[1]benzopyrano-[3,2-c][2]-benzopyran-7(5H)-one (2), 1,10-dihydroxy-8,9-dimethoxy-[1]benzopyrano-[3,2-c][2]-benzopyran-7(5H)-one (3), 1,8-dihydroxy-9,10-methylenedioxy-[1]benzopyrano-[3,2-c][2]-benzopyran-7(5H)-one (4), and 1,8,11-trihydroxy-9,10-methylenedioxy-[1]benzopyrano-[3,2-c][2]-benzopyran-7(5H)-one (5). The structure of irisoid B (2) was established unambiguously by X-ray diffraction study.

Key words *Iris bungei*; Iridaceae; peltogynoid; X-ray structure

Iris bungei MAXIM. (family Iridaceae) has been used in Mongolian traditional medicine for the treatment of various diseases, such as bacterial infections, cancer, and inflammation. Some benzoquinones isolated from *Iris* species have been used as anticancer agents in modern Chinese medicine.^{2,3)} This paper describes the isolation and characterization of five new peltogynoids (1—5) from the underground parts of *Iris bungei*. Although peltogynoids have been isolated from several genera of the family Leguminosae,^{4–12)} this is the first report of the isolation of peltogynoids from the family Iridaceae and the first X-ray structure determination of peltogynoid-type compounds.

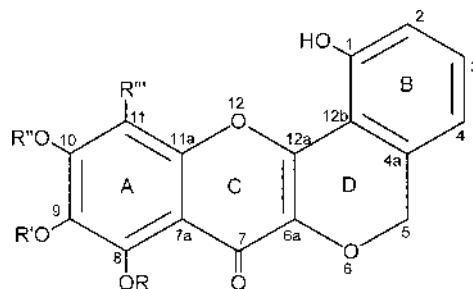
Results and Discussion

The methanolic extract of the underground parts of *I. bungei* was subjected to repeated column and preparative thin-layer chromatography to obtain compounds 1—5. Irisoid A (1) was isolated as a yellow amorphous powder. The high-resolution electron impact mass spectrum (HREI-MS) of 1 showed the $[M]^+$ at m/z 328.0597, in agreement with the molecular formula $C_{17}H_{12}O_7$ (Calcd 328.0583), indicating 12 degrees of unsaturation. Strong IR absorptions at 1652 (C=O) and 1628 cm^{-1} (C=C) along with UV bands at 350 ($\log \epsilon$ 3.93), 278 ($\log \epsilon$ 4.03), and 203 ($\log \epsilon$ 4.26) indicated that the compound has a flavone-type skeleton with oxygenation at the C-6a position.¹³⁾ Typical fragment ions appeared in EI-MS at m/z 313, 182, and 146, indicating the presence of a methoxyl group at C-9 with two hydroxyl groups in ring A, and only one hydroxyl group in ring B (Fig. 1).

The 1H -NMR spectrum (C_5D_5N , 400 MHz) of 1 showed two sets of signals for a total of four aromatic protons, along with signals for one *O*-methylene and one methoxyl group (Table 1). This revealed the presence of two independent aromatic spin systems in the molecule. A singlet at δ 6.98 corresponded to the H-11 of ring A. Three signals at δ 7.19 (br d, $J_{2,3}=8.3$ Hz), 7.29 (dd, $J_{3,2}=8.3$ Hz and $J_{3,4}=7.3$ Hz) and 6.70 (br d, $J_{4,3}=7.3$ Hz) were assigned to the aromatic H-2, H-3, and H-4 protons, respectively. This assignment indicated the presence of substituents at C-1 and C-4a of the aromatic ring B. Two downfield methylene protons resonated as a singlet at δ 5.13 (H-5), indicating the presence of an ethereal oxygen

and aromatic moiety vicinal to the methylene carbon. A methoxyl methyl appeared as a singlet at δ 3.93 substituted at C-9 of ring A. The appearance of a downfield singlet at δ 12.82 when the 1H -NMR was recorded in dimethyl sulfoxide ($DMSO$ - d_6) confirmed the presence of the OH group at C-8, which is involved in the hydrogen bonding with carbonyl group at C-7.

The broad-band (BB) decoupled ^{13}C -NMR spectrum of 1 showed resonances for all 17 carbons in the molecule (Table 1). The audited distortionless enhancement by polarization transfer (ADEPT) spectrum revealed the presence of one methyl, one methylene, four methines, and 11 quaternary carbons. The carbonyl carbons appeared in the most downfielded region at δ 175.4, whereas the other important signal at δ 68.8 was assigned to methylene C-5 and is involved in ether linkage with C-6a, which itself resonated at δ 135.9. The 1H - 1H and 1H - ^{13}C correlations were determined by 2D correlation spectroscopy (COSY-45°) and heteronuclear multiple quantum coherence (HMQC) experiments, respectively. All the 1H - and ^{13}C -NMR assignments were further confirmed by heteronuclear multiple-bond connectivity (HMBC) experiments (Fig. 2). The most important connectivities in the HMBC spectra were between H-11 (δ 6.98) with C-9 (δ 132.2), C-10 (δ 158.6), C-11a (δ 152.4) and C-7a (δ 106.1)



1 R = R'' = R''' = H, R' = CH₃

2 R = R'' = H, R' = R''' = CH₃

3 R = R' = CH₃, R'' = R''' = H

4 R = R'' = H, R' + R''' = -CH₂-

5 R = H, R' + R''' = -CH₂-, R'' = OH

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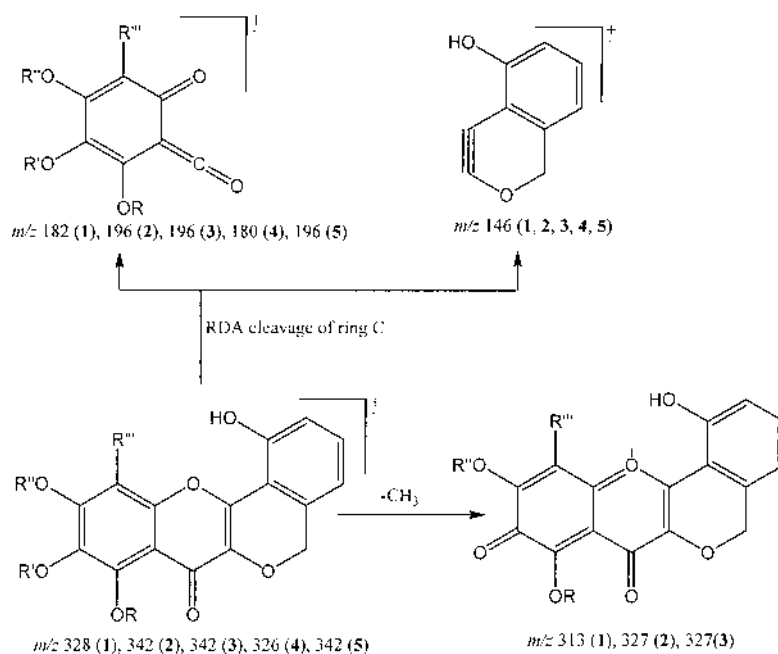


Fig. 1. Some Important EI-MS Fragments

Table 1. ^1H - and ^{13}C -NMR Spectral Data of Compounds 1—5

Position	1			2			3			4			5
	^1H -NMR δ_{H}		^{13}C -NMR δ_{C}	^1H -NMR δ_{H}		^{13}C -NMR δ_{C}	^1H -NMR δ_{H}		^1H -NMR δ_{H}		^{13}C -NMR δ_{C}	^1H -NMR δ_{H}	
	DMSO- d_6	$\text{C}_5\text{D}_5\text{N}$	$\text{C}_5\text{D}_5\text{N}$	DMSO- d_6	$\text{C}_5\text{D}_5\text{N}$	$\text{C}_5\text{D}_5\text{N}$	DMSO- d_6	$\text{C}_5\text{D}_5\text{N}$	DMSO- d_6	$\text{C}_5\text{D}_5\text{N}$	$\text{C}_5\text{D}_5\text{N}$	DMSO- d_6	
1	—	—	156.2	—	—	157.1	—	—	—	—	165.3	—	
2	6.96 (d)	7.19 (br d)	118.2	6.89 (d)	7.17 (br d)	118.4	6.96 (d)	7.19 (br d)	6.96 (d)	7.18 (br d)	118.0	6.85 (d)	
		$J_{2,3}=8.33$ Hz			$J_{2,3}=8.35$ Hz			$J_{2,3}=8.32$ Hz		$J_{2,3}=8.34$ Hz			
3	7.33 (t)	7.29 (dd)	132.9	7.24 (t)	7.26 (dd)	133.1	7.34 (t)	7.32 (dd)	7.32 (t)	7.31 (dd)	133.1	7.21 (t)	
		$J_{3,2}=8.33$ Hz			$J_{3,2}=8.35$ Hz			$J_{3,2}=8.32$ Hz		$J_{3,2}=8.34$ Hz			
		$J_{3,4}=7.38$ Hz			$J_{3,4}=7.37$ Hz			$J_{3,4}=7.38$ Hz		$J_{3,4}=7.37$ Hz			
4	6.75 (d)	6.70 (br d)	115.8	6.58 (d)	6.62 (br d)	115.3	6.75 (d)	6.72 (br d)	6.73 (d)	6.70 (br d)	115.7	6.54 (d)	
		$J_{4,3}=7.38$ Hz			$J_{4,3}=7.37$ Hz			$J_{4,3}=7.38$ Hz		$J_{4,3}=7.37$ Hz			
4a	—	—	136.0	—	—	136.2	—	—	—	—	136.1	—	
5	5.04 (s)	5.13 (s)	68.8	4.99 (s)	5.09 (s)	68.9	5.06 (s)	5.16 (s)	5.05 (s)	5.14 (s)	68.8	4.97 (s)	
6a	—	—	135.9	—	—	135.8	—	—	—	—	136.9	—	
7	—	—	175.4	—	—	175.4	—	—	—	—	175.4	—	
7a	—	—	106.1	—	—	107.2	—	—	—	—	108.0	—	
8	—	—	153.6	—	—	152.0	—	—	—	—	152.0	—	
9	—	—	132.2	—	—	138.0	—	—	—	—	142.2	—	
10	—	—	158.6	—	—	164.5	—	—	—	—	165.4	—	
11	6.45 (s)	6.98 (s)	95.3	6.58 (s)	6.85 (s)	91.5	6.68 (s)	6.97 (s)	6.74 (s)	6.81 (s)	89.7	—	
11a	—	—	152.4	—	—	153.1	—	—	—	—	154.1	—	
12a	—	—	150.8	—	—	151.1	—	—	—	—	150.2	—	
12b	—	—	112.4	—	—	112.4	—	—	—	—	112.0	—	
-OCH ₃	3.78 (s)	3.93 (s)	60.1	3.70 (s)	3.88 (s)	60.3	3.72 (s)	3.89 (s)	—	—	—	—	
-OCH ₃	—	—	—	3.85 (s)	4.08 (s)	55.6	3.92 (s)	4.14 (s)	—	—	—	—	
-OCH ₂ O	—	—	—	—	—	—	—	—	6.15 (s)	6.05 (s)	102.9	6.09 (s)	
8-OH	12.82 (s)	—	—	12.84	—	—	—	—	12.73	—	—	12.81	

of aromatic ring A. The aromatic protons of ring B also showed the following couplings: H-2 (δ 7.19) with C-12b (δ 112.4) and C-4 (δ 115.8); H-3 (δ 7.29) with C-1 (δ 156.2) and C-4a (δ 136.0); and H-4 (δ 6.70) with C-12b (δ 112.4), C-2 (δ 118.2) and C-5 (δ 68.8) of ring D. The H-5 methylene protons (δ 5.13) of ring D were found to be coupled with C-4 (δ 115.8), C-4a (δ 136.0), C-12b (δ 112.4), and C-6a (δ

135.9). Finally, the methoxyl protons (δ 3.93) were found to be coupled with C-9 (δ 132.2). On the basis of the above studies, the structure 1,8,10-trihydroxy-9-methoxy-[1]benzopyrano-[3,2-*c*][2]-benzopyran-7(5*H*)-one was deduced for compound **1**.

Irisoid B (**2**), $\text{C}_{18}\text{H}_{14}\text{O}_7$, exhibited a ^1H -NMR spectrum that closely resembled that of **1**, with the major difference

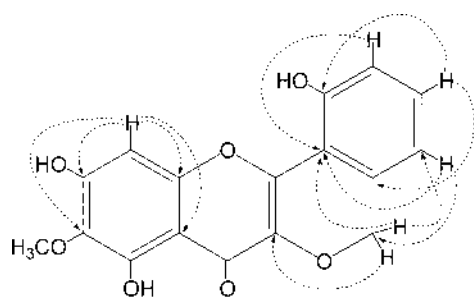


Fig. 2. Important HMBC Interactions in Compound 1

being the presence of an additional methoxyl group singlet at δ 4.08 (Table 1). The mass fragment at m/z 196 in the EIMS indicated the presence of an additional methoxyl group in ring A, and the fragment resulted from the retro Diels–Alder cleavage of ring C (Fig. 1). The ^{13}C -NMR spectrum of **2** also had one more methoxyl carbon signal at δ 55.6. The downfield chemical shift of C-10 (δ 164.5) (as compared with C-10 of compound **1**, which resonated at δ 158.6), indicated that the second methoxyl group is substituted at C-10 of ring A. The position of the second methoxyl was further confirmed by the nuclear Overhauser effect (NOE) experiments. Irradiation of the methoxyl protons (δ 4.08) resulted in a significant enhancement of the H-11 proton (δ 6.85). The MS, ^1H -NMR, ^{13}C -NMR, and NOE spectra of **2** indicated that compound **2** is 1,8-dihydroxy-9,10-dimethoxy-[1]benzopyrano-[3,2-*c*][2]-benzopyran-7(*5H*)-one. Subsequent single-crystal X-ray diffraction analysis (Fig. 3, Table 2) unambiguously confirmed the structure of compound **2**. The molecule **2** showed planarity throughout the structure, with only the O–C bond in ring D being slightly above the plane. The hydrogen bonding between the phenolic hydroxyl group at the C-8 position of ring A and the oxygen of the C-7 ketone carbonyl was also apparent in the X-ray structure. The average C–C bond distance in the aromatic ring was 1.386(2) Å.¹⁴

Irisoid C (**3**), $\text{C}_{18}\text{H}_{14}\text{O}_7$, showed almost the same ^1H -NMR spectrum as that of **2**, only being differentiated by the absence of the OH of the C-8 proton signal in $\text{DMSO-}d_6$ and the presence of a methoxyl group signal at δ 4.14, which indicated the presence of a methoxyl group at C-8 (Table 1). The positions of the methoxyl groups were further confirmed by NOE experiments. Irradiation of either methoxyl group signal did not affect any aromatic proton, which indicated that the methoxyl groups are located at C-8 and C-9 of ring A. These spectroscopic observations permitted the assignment of the structure 1,10-dihydroxy-8,9-dimethoxy-[1]benzopyrano-[3,2-*c*][2]-benzopyran-7(*5H*)-one to compound **3**.

Compound **4** (irisoid D), $\text{C}_{17}\text{H}_{10}\text{O}_7$, exhibited a ^1H -NMR spectrum which closely resembled those of **1** and **2**. The major differences were the absence of the methoxyl group signals and presence of one methylenedioxy signal at δ 6.15 as a singlet, with the carbon atom resonating at δ 102.9 in the ^{13}C -NMR spectrum (Table 1). The position of the methylenedioxy group was assigned to ring A by the fragment ion appearing at m/z 180 in the EI-MS spectrum, resulting from the retro Diels–Alder cleavage of ring C (Fig. 1). Finally its position was confirmed at C-9 and C-10 by the downfield chemical shifts of C-9 (δ 142.2) and C-10 (δ 165.4) in the ^{13}C -NMR spectrum as compared with compound **1** (Table 1).

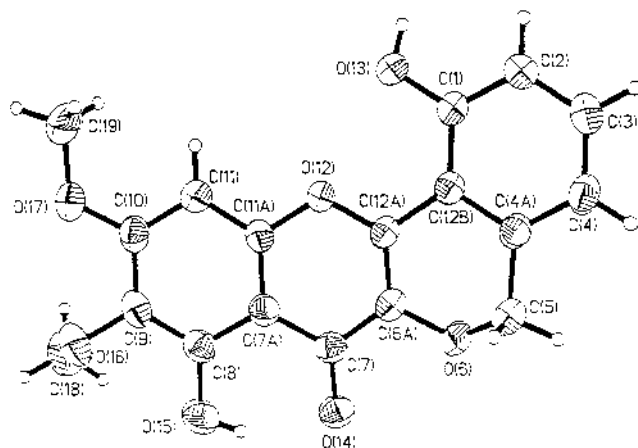


Fig. 3. A Computer-Generated ORTEP Drawing of the X-ray Structure of Compound 2

Table 2. Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$\text{\AA}^2 \times 10^3$] for Irisoid B (**2**)

	x	y	z	U (eq)
C (1)	4641 (2)	2116 (1)	7949 (1)	41 (1)
C (2)	6347 (3)	1700 (1)	8053 (2)	49 (1)
C (3)	7401 (3)	1714 (1)	8965 (2)	53 (1)
C (4)	6797 (3)	2139 (1)	9799 (2)	48 (1)
C (4A)	5130 (2)	2571 (1)	9706 (1)	39 (1)
C (5)	4476 (3)	3084 (1)	10565 (1)	46 (1)
O (6)	2464 (2)	3050 (1)	10594 (1)	46 (1)
C (6A)	1591 (2)	3275 (1)	9680 (1)	38 (1)
C (7)	-73 (2)	3763 (1)	9706 (1)	38 (1)
C (7A)	-887 (2)	4002 (1)	8722 (1)	37 (1)
C (8)	-2460 (2)	4541 (1)	8616 (1)	40 (1)
C (9)	-3205 (2)	4758 (1)	7665 (2)	43 (1)
C (10)	-2454 (2)	4429 (1)	6790 (1)	42 (1)
C (11)	-899 (2)	3916 (1)	6867 (1)	42 (1)
C (11A)	-150 (2)	3719 (1)	7832 (1)	37 (1)
O (12)	1414 (2)	3225 (1)	7869 (1)	40 (1)
C (12A)	2281 (2)	3031 (1)	8787 (1)	36 (1)
C (12B)	4023 (2)	2566 (1)	8780 (1)	37 (1)
O (13)	3553 (2)	2087 (1)	7070 (1)	54 (1)
O (14)	-754 (2)	3973 (1)	10528 (1)	47 (1)
O (15)	-3215 (2)	4854 (1)	9446 (1)	54 (1)
O (16)	-4646 (2)	5323 (1)	7551 (1)	52 (1)
O (17)	-3342 (2)	4657 (1)	5895 (1)	54 (1)
C (18)	-6435 (2)	4981 (1)	7692 (2)	64 (1)
C (19)	-2733 (2)	4311 (1)	4984 (1)	71 (1)

U (eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

On the basis of these data, the structure 1,8-dihydroxy-9,10-methylenedioxy-[1]benzopyrano-[3,2-*c*][2]-benzopyran-7(*5H*)-one was assigned to new compound **4**.

The ^1H -NMR spectrum of irisoid E (**5**), $\text{C}_{17}\text{H}_{10}\text{O}_8$, resembled that of **4**, with the major difference being the absence of the H-11 signal, which indicated that the C-11 position was substituted (Table 1). The mass fragment at m/z 196 indicated an additional hydroxyl group in ring A, resulting from the retro Diels–Alder cleavage of ring C (Fig. 1). The unreactivity of compound **5** with CH_2Cl_2 in CsF and DMF confirmed the absence of two vicinal phenolic hydroxyl groups in **5**.¹⁵ Therefore the positions of hydroxyl groups in ring A were inferred at C-8 and C-11. The proton of C-8 OH appeared downfield at δ 12.86 due to hydrogen bonding with C-7 carbonyl when the ^1H -NMR spectrum was recorded in

DMSO- d_6 . The position of the methylenedioxy group was inferred between C-9 and C-10. The spectroscopic data and the negative result of the methylenation reaction permitted the assignment of the structure 1,8,11-trihydroxy-9,10-methylenedioxy-[1]benzopyrano-[3,2-c][2]-benzopyran-7(5H)-one to compound **5**.

Experimental

General Melting points (corrected and uncorrected) were determined in glass capillary tubes using a Buchi 535 melting point apparatus. The UV spectra were measured on a Hitachi U-3200 spectrophotometer. The IR spectra were recorded on a Jasco A-302 spectrophotometer. The $^1\text{H-NMR}$ spectra were recorded on Bruker AM 400 and AMX 500 NMR spectrometers using a UNIX data system at 400 and 500 MHz, respectively, while $^{13}\text{C-NMR}$ spectra were recorded at 100 and 125 MHz on the same instruments using the solvent DMSO- d_6 and $\text{C}_5\text{D}_5\text{N}$. The LREI-MS and HREI-MS were recorded on a Jeol JMS HX 110 mass spectrometer with a DA 5000 data system.

Plant Material The underground parts of *I. bungei* were collected in September 1997 from Choir Somone, in the Dornogov area of Mongolia. A herbarium specimen of this plant (voucher no. N659) has been deposited at the Botanical Institute of the Mongolian Academy of Sciences, Ulaanbaatar, Mongolia.

Extraction and Isolation The underground dried plant material (100 g) was extracted with methanol at room temperature for 2 weeks and the resulting extract was concentrated to a gum (8 g). This gum was loaded onto a Silica gel (150 g) column and eluted with CHCl_3 to afford pure compound irisoid A (**1**) (54 mg, $R_f=0.43$) along with a yellow fraction (148 mg). This fraction was also loaded onto a Silica gel column (25 g) and the column was eluted with CHCl_3 . This yielded two fractions which were then subjected to preparative TLC in CHCl_3 -hexane (8:2) to obtain irisoids B (**2**) (7.2 mg, $R_f=0.49$), C (**3**) (3.4 mg, $R_f=0.53$), D (**4**) (8.5 mg, $R_f=0.64$), and E (**5**) (3.2 mg, $R_f=0.46$) along with some known flavones and isoflavones.

Irisoid A (1) Amorphous powder, UV λ_{max} (MeOH) (log ϵ): 350.4 (3.93), 278.0 (4.03), 203 nm (4.26); IR ν_{max} (KBr): 3240 (OH), 2925 (CH), 1652 (C=O), 1628 (C=C), 1588 (C=C), 1197 (C-O) cm^{-1} . $^1\text{H-}$ and $^{13}\text{C-NMR}$ data: Table 1; EI-MS m/z : 328 (100), 313 (91), 285 (84), 183 (38), 182 (14), 146 (19), and 145 (44); HREI-MS m/z : 328.0597 (Calcd 328.0583).

Irisoid B (2) Yellow needles, mp 329–330 °C, UV λ_{max} (MeOH) (log ϵ): 353 (3.86), 273 (4.05), 202 nm (4.34); IR ν_{max} (KBr): 3250 (OH), 2910 (CH), 1648 (C=O), 1631 (C=C), 1592 (Ar. C=C), 1215 (C-O) cm^{-1} . $^1\text{H-}$ and $^{13}\text{C-NMR}$ data: Table 1; EI-MS m/z : 342 (100), 327 (90), 299 (73), 197 (41), 196 (17), 146 (22), and 145 (45); HREI-MS m/z : 342.0701 (Calcd 342.0739).

Crystal Data and X-Ray Crystal Structure Determination of Irisoid B (2) Crystals of **2** suitable for X-ray diffraction analysis were obtained by recrystallization from DMSO- d_6 . Crystal Data: Light yellow prismatic crystals, dimensions 0.25×0.2×0.31 mm³, $\text{C}_{18}\text{H}_{14}\text{O}_7$; M, 342.29 amu; Monoclinic, $\beta=93.77(2)^\circ$, $a=7.1680(10)$, $b=16.178(3)$, $c=13.132(3)\text{Å}$, $V=1519.5(5)\text{Å}^3$. Space group $P2_1/n$, $Z=2$, $D_x=0.748\text{Mg m}^{-3}$, $\mu=0.494\text{mm}^{-1}$, $F(000)=356$; temperature=293 K.

Data Collection: Bruker P4 diffractometer (previously Nicolet), θ - 2θ scan type, graphite-monochromated $\text{CuK}\alpha$ radiations; 5930 reflections were measured ($3.5 < \theta < 135^\circ$), of which 2626 were unique. Three standard reflections were measured after every 97 reflections which showed no significant crystal decay. Data were corrected for Lorentz and polarization effects.

Structure Analysis and Refinement: The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 values. Non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included at calculated positions and refined in the riding mode. Final values of the residuals R and wR_2 [for 2626 reflections with $I > 2\sigma(I)$] were, respectively, 0.0438 and 0.1240. The highest and lowest peaks in final

difference Fourier map were 0.242 and -0.189eÅ^{-3} .¹⁴

Irisoid C (3) Amorphous powder, UV λ_{max} (MeOH) (log ϵ): 359 (3.51), 280 (3.52), 212 (3.84), 202 nm (3.88); IR ν_{max} (KBr): 3310 (OH), 2925 (CH), 1646 (C=O), 1631 (C=C), 1585 (C=C), 1208 (C-O) cm^{-1} ; $^1\text{H-NMR}$ data: Table 1; EI-MS m/z : 342 (100), 327 (81), 299 (79), 197 (33), 196 (23), 146 (17), and 145 (37); HREI-MS m/z : 342.0812 (Calcd 342.0739).

Irisoid D (4) Amorphous powder, UV λ_{max} (MeOH) (log ϵ): 363 (3.48), 278 (3.57), 212 nm (3.82); IR ν_{max} (KBr): 3285 (OH), 2910 (CH), 1648 (C=O), 1633 (C=C), 1580 (Ar. C=C), 1205 (C-O) cm^{-1} ; $^1\text{H-}$ and $^{13}\text{C-NMR}$ data: Table 1; EI-MS m/z : 326 (100), 298 (34), 181 (39), 180 (28), 146 (21), and 145 (33); HREI-MS m/z : 326.0383 (Calcd 326.0427).

Irisoid E (5) Amorphous powder, UV λ_{max} (MeOH) (log ϵ): 362 (3.38), 274 (3.56), 210 nm (3.73); IR ν_{max} (KBr): 3275 (OH), 2915 (CH), 1645 (C=O), 1630 (C=C), 1582 (Ar. C=C), 1208 (C-O) cm^{-1} ; $^1\text{H-NMR}$ data: Table 1; EI-MS: m/z : 342 (100), 314 (42), 197 (54), 196 (34), 146 (26), and 145 (44). HREI-MS m/z : 342.0268 (Calcd 328.0376).

Methylenation Reaction on 5 The relative positions of the methylenedioxy group and hydroxyl groups were confirmed by performing the methylenation reaction.¹⁵ A solution of **5** (0.05 mol) in anhydrous DMF was shaken with anhydrous cesium fluoride (CsF) and then CH_2Cl_2 (0.011 mol) was added to the solution. The reaction mixture was heated with stirring at 110–120 °C for 1.5 h and then subjected to solvent-solvent extraction with diethylether and water. The ether layer was separated and washed with water to remove the *N,N*-dimethylformamide (DMF) completely with dilute NaOH. The TLC and EI-MS of the isolated component showed that no reaction occurred.

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References and Notes

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