15,21-Cyclowithanolides from *Jaborosa bergii*

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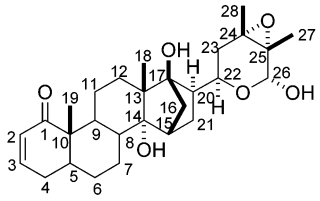
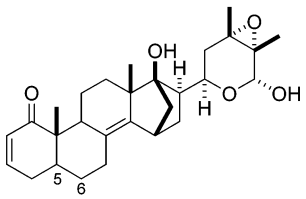
Six new withanolides (**1**−**6**) were isolated from the aerial parts of *Jaborosa bergii* plants and characterized by spectroscopic methods (1D and 2D NMR, MS). Five of the new compounds presented a novel norbornane-type structure in ring D of the steroid nucleus (**1**−**5**), resulting from a carbon−carbon bond between C-15 and C-21. The sixth withanolide isolated was the 5α-chloro-6*β*-hydroxy analogue (**6**) of 2,3-dehydrojaborosalactol M (**7**), previously isolated from this plant. Compound **1** showed selective phytotoxicity toward monocotiledoneous and dicotiledoneous species.

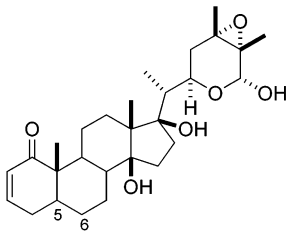
Withanolides, a group of oxygenated steroidal lactones of the ergostane type, have been isolated from 18 genera of the Solanaceae family, a species of *Ajuga* genus (Labiatae), and a species of *Cassia* genus (Leguminosae).[1] Many of these compounds exhibit interesting biological activities such as antifeedant, insecticide, and immunosuppressive properties, and they are inducers of the enzyme quinone reductase.[2] Recently withanolides isolated from *Iochroma australe* showed phytotoxic activity on crop and weed species, as well as selective effects on germination and radicle growth.[3]



1 5β,6β-epoxy
5 5α-Cl, 6β-OH



2 5β,6β-epoxy
3 5α-OH, 6β-OH
4 5α-Cl, 6β-OH



6 5α-Cl, 6β-OH
7 5β,6β-epoxy

Jaborosa Miers is a South American genus belonging to the Solanaceae family that comprises about 23 species,[4] 11 of which are almost exclusively distributed in Argentina. Previous studies on a population of *J. bergii* Hieron. growing in San Luis Province, Argentina, yielded five new withanolides with the unusual feature of having hydroxyl groups at position C-14 and C-17 both with *β*-configuration.[5] Continuing our studies of withanolides from species of the *Jaborosa* genus,[6] we reinvestigated *J. bergii* and now report on the isolation of six new withanolides, **1**−**6**, and 2,3-dehydrojaborosalactol M (**7**).

Results and Discussion

Withanolides **1**−**7** were obtained by ethanolic extraction of the aerial parts of *J. bergii* followed by silica gel column chromatography and preparative TLC. Compound **1** revealed a molecular formula of $C_{28}H_{38}O_7$ by HRCIMS. The ^{1}H NMR spectrum of **1** (Table 1) showed the characteristic chemical shifts and multiplicities for the 1-oxo-2-ene system at ring A, where signals for H-2 and H-3 were clearly distinguished at *δ* 6.03 and 6.87, respectively. The correlations observed in the COSY experiment between the pairs H-2/H-4*β*, H-3/H-4α, and H-3/H-4*β* led to the assignment of H-4*β* and H-4α at *δ* 2.97 and 1.95, respectively. The doublet at *δ* 3.23 was consistent with a 5*β*,6*β*-epoxy group, also supported by the small value of the coupling constant between H-6*β* and H-7*β* (J = 2.3 Hz). The broad singlet at *δ* 5.02 (H-26) together with the two three-proton singlets at *δ* 1.41 (H_3-27) and 1.39 (H_3-28) and a doublet of triplets at *δ* 3.95 (H-22), indicated the presence of a six-membered epoxy lactol ring as side chain. The chemical shifts and coupling constants involved in the signals corresponding to H-22, H-26, H-27, and H-28 were consistent with the proposed stereochemistry.[5]

The ^{1}H chemical shift of the angular methyl group H_3-18 (*δ* 1.06, s) was indicative of a hydroxyl group with *β*-configuration at C-17 and/or C-14.[5] The presence of two hydroxyls was confirmed by the quaternary carbon resonances at *δ* 87.2 (C-17) and 80.9 (C-14) (Table 2). The ^{1}H NMR spectrum did not show a signal corresponding to the 21-methyl, which at first glance led us to suspect that C-21 contained an oxygenated function. However, no oxygenated methylene resonances were observed in the ^{1}H and ^{13}C NMR (DEPT) spectra. The possibility of a carbonyl group

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Table 1. ^{1}H NMR Spectral Data of Compounds **1**−**6** in Cl_3CD[a]

H	**1**[b]	**2**[b]	**3**[c]	**4**[b]	**5**[c]	**6**[b]
2	6.03 dd (10.0; 2.5)	6.10 dd (10.0; 2.9)	5.92 dd (10.0; 2.6)	5.97 dd (10.2; 2.1)	5.95 dd (10.2; 2.6)	5.94 dd (10.2; 2.3)
3	6.87 ddd (10.0; 6.1; 2.3)	6.87 ddd (10.0; 6.6; 2.3)	6.65 ddd (10.0; 4.9; 1.8)	6.68 ddd (10.2; 5.1; 2.3)	6.69 ddd (10.2; 5.1; 2.0)	6.67 ddd (10.2; 5.0; 2.3)
4α	1.95 dd (19.3; 6.1)	1.92 dd (18.4; 6.6)	2.12 dd (20.1; 4.9)	2.57 ddd (20.4; 5.1; 1.0)	2.52 dd (20.1; 5.1)	2.52 dd (20.0; 5.0)
4*β*	2.97 dt (19.3; 2.5)	2.94 dt (18.4; 2.6)	3.33 br t (20.1)	3.56 dt (20.4; 2.1)	3.51 dt (20.1; 2.6)	3.52 dt (20.0; 2.3)
6	3.23 d (2.3)	3.11 br s	3.56 br s	3.94 br s	4.08 br s	4.08 br s
7α	1.69 t (ca. 13)	2.19 br d (15.9)	2.35 dd (14.2; 2.2)	2.43 dd (14.8; 2.7)	1.87 m	1.98 m
7*β*	2.34 dt (13.4; 2.5)	2.82 dd (15.9; 2.2)	2.56 dd (14.0; 2.6)	2.85 dd (14.8; 2.3)	2.33 m	2.15 m
8	1.74 td (11.9; 2.5)					1.95 m
9	1.39 m	2.14 t (9.0)	2.86 t (8.4)	2.97 br t (8.7)		2.05 m
11α	2.14 dq (12.9; 4.3)	1.92 m	2.56 m	2.61 dq (14.3; 3.2)		2.23 dq (12.0; 3.3)
11*β*	1.29 dq (3.4; 12.9)	1.92 m	1.67 m	1.65 dq (2.7; 10.5)		1.20 m
12α	1.79 m	1.37 m	1.42 m	1.42 m		1.52 m
12*β*	1.47 m	1.31 m	1.42 m	1.42 m		1.27 m
15	1.83 br d (5.9)	2.63 br s	2.70 br s	2.68 br s		2.15 m and 1.77 dd (10.7; 5.2)
16α	1.47 br d (10.2)	1.35 br d (9.6)	1.36 br d (10.6)	1.37 br d (9.8)		1.86 dd (14.2; 4.2)
16*β*	2.07 br d (10.0)	2.07 br d (9.6)	2.05 br d (10.6)	2.08 br d (9.8)		2.04 m
18	1.06 s	1.13 s	1.11 s	1.13 s	1.10 s	1.11 s
19	1.25 s	1.22 s	1.20 s	1.26 s	1.33 s	1.38 s
20	2.03 m	1.80 m	1.87 m	1.87 m		1.93 m
21	H-α 1.51 m H-*β* 1.08 ddd (13.8; 5.5; 3.2)	H-α 1.22 m H-*β* 1.22 m	H-α 1.27 m H-*β* 1.27 m	H-α 1.32 td (8.2; 2.5) H-*β* 1.22 m		0.97 d (7.1)
22	3.95 dt (2.2; ca. 10.5)	3.88 dt (2.2; ca. 10.5)	3.93 dt (2.6; ca. 10.0)	3.86 dt (2.5; 11.4)	3.97 dt (2.2; 10.2)	4.03 m
23α (equat)	2.01 dd (14.4; 2.2)	1.98 dd (14.6; 2.3)	1.99 dd (14.6; 2.2)	1.99 dd (14.6; 2.3)	2.00 m	2.12 dd (14.4; 2.9)
23*β* (axial)	1.54 dd (14.4; 11.1)	1.50 dd (14.6; 11.1)	1.51 dd (14.6; 11.0)	1.55 m	1.61 dd (14.4; 11.1)	1.72 dd (14.8; 11.6)
26	5.02 br s	5.01 br s	5.04 s	5.02 s	5.03 br s	5.01 br s
27	1.41 s	1.41 s	1.41 s	1.43 s	1.42 s	1.41 s
28	1.39 s	1.38 s	1.39 s	1.40 s	1.40 s	1.40 s

[a] Chemicals shifts (*δ*) downfield from TMS, *J* couplings (in parentheses) in Hz. [b] 500.13 MHz. [c] 200.13 MHz.

at C-21 was also ruled out, as the ^{13}C NMR spectrum showed a single carbonyl resonance at *δ* 203.7 assigned to C-1.

In the COSY experiment the H-22 resonance (*δ* 3.95) showed only two correlation peaks with resonances at *δ* 1.54 (H-23*β*) and 2.00−2.03, the latter corresponding to the partially overlapping signals of H-20 and H-23*β*. A relayed COSY experiment allowed correlation of H-22 with H-21*β* (*δ* 1.08) from which H-20 (*δ* 2.03) and H-21α (*δ* 1.51) could be assigned. Surprisingly, the spin system did not finish in H-21, but showed continuity through H-15 (*δ* 1.83) and ended with the signals corresponding to H-16*β* (*δ* 2.07) and H-16α (*δ* 1.47). This evidence led us to propose a carbon−carbon bond between C-21 and C-15, resulting in a norbornane-type structural moiety. A bond between C-21 and C-16 that would give a cyclobutane ring and show an equivalent spin pattern was ruled out by a HMBC experiment. In this experiment the signal corresponding to H-21 showed three-bond cross-correlation peaks with C-17 and C-14; the latter would not be observed if the C−C bond was between C-21 and C-16. The key correlations observed in the HMBC experiment are shown in Figure 1. The full and unambiguous proton and carbon NMR assignments were completed using a combination of DEPT, COSY, relayed COSY, NOESY, HSQC, and HMBC experiments.

Assuming the *β*-orientation of the hydroxyl at C-17, the additional ring should arise upon cyclization of C-21 on the α-face of ring D. This was confirmed by the strong cross-correlation peak between H-16*β* and H_3-18 in the NOESY experiment (Supporting Information). Also, the NOE correlation observed for the pair H-12α/H-20 indicated the 20-*R* stereochemistry. The large coupling between H-22 and H-20 (ca. 10.5 Hz) was indicative of a predominant rotamer around the C-20−C-22 bond with an *anti* arrangement for these hydrogens, thus the simultaneous NOE correlations for the pairs H-22/H-16α and H-23α/H-21*β* in this rotamer are possible only for the *R* configuration at C-22. The α-orientation of the 14-hydroxyl was established from the weak NOE correlation of H_3-18 and H_3-19 and the absence of NOE between H-21α and H-7α, H-9α, and H-12α. (See Supporting Information for an AM1 calculated structure showing the spatial arrangement that gives rise to the observed NOE correlations.) The chemical shift of C-14 (80.8 ppm) supported this stereochemical assignment.[7]

The HREIMS of compound **2** displayed a molecular ion at *m*/*z* 468.2513, 18 Da less than compound **1**. The ^{13}C NMR

Table 2. ^{13}C NMR Spectral Data of Compounds **1**−**4** and **6** in Cl_3CD[a]

C	**1**[b]	**2**[c]	**3**[c]	**4**[b]	**6**[c]
1	203.8	202.5	204.3	200.7	201.2
2	129.1	129.8	128.7	128.8	128.5
3	144.9	143.9	141.9	141.6	141.7
4	32.9	32.6	35.7	37.3	37.2
5	61.5	62.2	77.3	80.5	80.0
6	64.2	63.3	75.0	75.4	74.5
7	26.7	29.6	32.7	33.1	28.2
8	41.2	120.3	122.5	121.3	35.5
9	43.2	41.0	38.2	38.9[d]	37.6
10	48.7	45.8	45.3	45.6	52.5
11	24.5	21.0	20.8	21.1	22.8
12	31.2	28.0	27.5	27.4	32.7
13	46.4	50.8	54.1	54.6	51.4
14	80.8	148.4	148.8	150.7	86.9
15	42.4	35.6	35.4	35.6	30.9
16	36.6	38.3	37.9	38.2	34.8
17	87.3	87.5	87.4	87.3	89.7
18	20.4	21.3	20.9	21.0	14.2
19	14.9	14.5	16.1	17.1	16.5
20	41.0	39.0	38.8	39.5[d]	40.8
21	24.8	35.2	36.2	36.3	11.3
22	68.1	67.3	67.5	67.2	65.0
23	34.7	34.5	34.6	34.5	32.9
24	63.4	63.4[d]	63.3	64.5	67.2
25	63.3	63.9[d]	63.1	63.6	63.3
26	91.5	91.5	91.4	91.5	91.7
27	16.6	16.4	16.4	16.4	16.5
28	18.5	18.6	18.4	18.6	18.8

[a] Chemical shifts (δ) downfield from TMS. [b] 125.77 MHz. [c] 50.32 MHz. [d] Assignments may be interchanged.

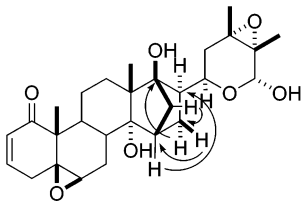

Figure 1. Relevant correlations in the HMBC spectrum of **1**.

spectrum of **2** (Table 2) did not present the oxygenated carbon signal corresponding to C-14, but showed two extra nonprotonated olefinic carbon signals at δ 121.3 and 150.7 suggesting that compound **2** was the dehydration product of **1** with the double bond located either at C-8/C-14 or at C-14/C-15. 14α-Hydroxywithanolides are known to dehydrate readily to give a mixture of $\Delta^{8(14)}$ and Δ^{14} unsaturated derivatives;[8] in the case of **1**, due to C-15 being a bridgehead carbon, the formation of the latter olefinic bond is unlikely. The COSY experiment revealed the same spin system involving H-15, H-16, H-20, H-21, H-22, and H-23 as for compound **1**, supporting the location of the double bond at C-8/C-14. When compared with compound **1**, the presence of this double bond produced a significant deshielding effect on the protons at neighboring carbons (H-7α, H-7β, H-9, and H-15) and a sizable shielding of spatially close protons in the α-face of the molecule (H-12α, H-20, H-21α) (Table 1). The complete proton and carbon NMR assignments of **2** were achieved using a combination of DEPT, COSY, and HETCOR spectra.

Compound **3** revealed a molecular formula of $C_{28}H_{38}O_7$ by HREIMS, its ^1H and ^{13}C NMR spectra being very similar to those of **2** (Tables 1 and 2). The ^{13}C NMR spectrum indicated that the only difference between **2** and **3** was the substitution pattern at C-5 and C-6. Instead of the signals of the epoxy group at δ 62.2 (C-5) and 63.3 (C-6) in **2**, the spectrum of **3** showed two signals at δ 77.3 (C-5) and 75.0 (C-6) typical of a 5α,6β-diol.[6] The multiplicity and the chemical shift of H-6 (δ 3.56, t, J = 2.5 Hz) were in good agreement with the β-orientation of the hydroxy group at C-6. Spectral NMR assignments were confirmed by DEPT, COSY, and HETCOR spectra.

The ^1H and ^{13}C NMR spectra of compound **4** were closely related to those of withanolide **3** with significant differences for the resonances of H-4 (α and β), H-6, H-19, and C-5 (Tables 1 and 2), suggesting again differences in the substitution pattern at C-5 and C-6. The unusually high chemical shift observed for H-4β (δ 3.56) in the ^1H NMR spectrum indicated a chlorine atom with α-orientation at C-5. The broad signal at δ 3.94 suggested the presence of a β-hydroxy group at C-6. The 5α-chloro-6β-hydroxy arrangement is a characteristic structural feature of several withanolides isolated from different species of the *Jaborosa* genus.[6,9] The substitution pattern in ring B was further corroborated by the signals at δ 80.5 and 75.4 in the ^{13}C NMR spectrum that were assigned to C-5 and C-6, respectively, and allow differentiation from the isomeric 5-hydroxy-6-chloro arrangement.[9,10] The NMR spectral assignments for **4** were confirmed by DEPT and COSY spectra. This compound decomposed on standing, possibly due to the simultaneous allylic/homoallylic nature of the clorohydrin moiety, which upon dehydration and HCl elimination gives a highly conjugated system involving rings A, B, and C. Together with **4** we isolated a withanolide, which was tentatively assigned as structure **5** on the basis of its ^1H NMR spectrum. This compound decomposed rapidly in solution to give **4**, and only partial data could be obtained from its COSY spectrum. However, the chemical shifts of the hydrogens at C-7 and of the angular methyl CH_3-19 (very similar to those of **1**) strongly suggested the presence of the 14α-hydroxyl.

Compound **6** revealed a molecular formula of $C_{28}H_{41}O_7Cl$ by HRFABMS. The ^1H and ^{13}C NMR spectra resembled those of 2,3-dehydrojaborosalactol M (**7**) previously isolated from *J. bergii*.[5] The only difference between compounds **6** and **7** is the substitution pattern at C-5 and C-6. As in the previous case, the unusually high chemical shift observed for proton H-4β (δ 3.52) in the ^1H NMR spectrum of **6** indicated a chlorine atom with α orientation at C-5. The broad signal at δ 4.08 suggested the presence of a β-hydroxy group at C-6. The substitution pattern in ring B was further corroborated by the signals at δ 79.9 and 74.5 in the ^{13}C NMR spectrum that were assigned to C-5 and C-6, respectively. The NMR spectral assignments for **6** were confirmed by DEPT, COSY, and HMQC experiments.

Previous work in our laboratory demonstrated that withanolides show selective phytotoxic effects on some monocotyledoneous and dicotyledoneous species.[3] To evaluate compound **1** as a potential phytotoxic agent, a number of bioassays were undertaken on two monocotyledoneous and three dicotyledoneous species. The effect produced by **1** on germination was not significant in the species assayed; however, significant inhibition of radicle growth was found at 2×10^{-3} M on the dicotyledoneous species *Chenopodium album*, *Ipomea purpurea*, and *Lactuca sativa* (phytogrowth inhibitory activity > 49%). The activity was nonsignificant at 2×10^{-5} M (<26%) (Figure 2). On the other hand, in the monocotiledoneous species tested the phytogrowth effect of compound **1** was stimulatory. *Zea mays* radicle growth values were significant ($p < 0.05$) and showed a good level of stimulatory activity (>112%) in the concentration range tested (Figure 2). Thus, **1** may act as a selective phytogrowth controller, stimulating radicle growth of monocotyledoneous species.

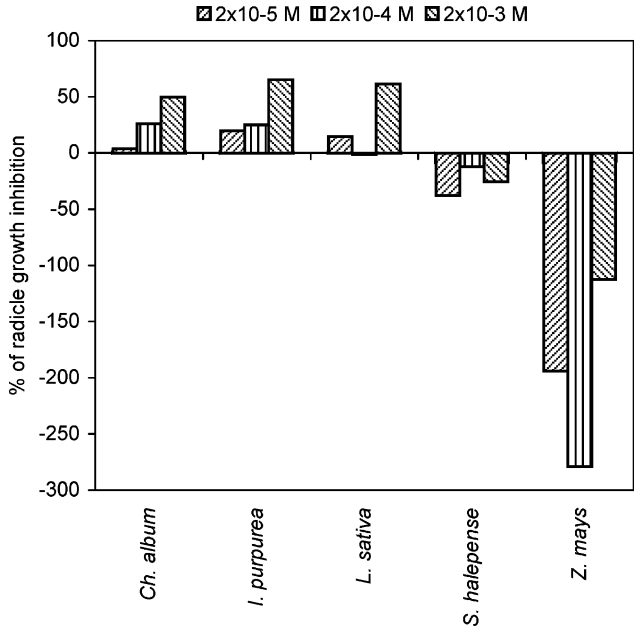

Figure 2. Effect of **1** at different concentrations on radicle growth of (a) dicotiledoneous species *Chenopodium album*, *Ipomea purpurea*, and *Lactuca sativa* (data at 2×10^{-3} M differ significantly from controls, $p < 0.05$) and (b) monocotiledoneous species *S. halepense* and *Zea mays* (data for the latter differ significantly from controls, $p < 0.05$). The data are presented as percentage differences from the control (zero value); positive values represent inhibition of the studied variable (radicle growth), and negative values represent stimulation.

Experimental Section

General Experimental Procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 NMR spectrometer at 200.13 (^{1}H) and 50.32 (^{13}C) MHz or a Bruker AM-500 at 500.13 (^{1}H) and 125.77 (^{13}C) MHz. Multiplicity determinations (DEPT) and 2D spectra (COSY, relayed COSY, and HETCOR) were obtained using standard Bruker software. HMBC, HSQC, and HMQC spectra were obtained in a Bruker DPX-300 spectrometer. Chemical shifts are given in ppm (δ) downfield from TMS internal standard. EIMS were collected on a Simadzu QP-5000 mass spectrometer at 70 eV by direct inlet; CIMS, HRCIMS, and HRFABMS were measured in a JEOL JMS AX-500 mass spectrometer. IR and UV spectra were obtained in Nicolet 5-SXC and Shimadzu-260 spectrophotometers, respectively. Melting points were measured on a mercury thermometer apparatus and are uncorrected. Optical rotations were measured on a Jasco P-1010 polarimeter. Column chromatography was performed on Kieselgel 60 (0.063−0.200 mm). TLC analysis was performed on Si gel 60 F_{254} (0.2 mm thick).

Plant Material. The aerial parts of *J. bergii* plants were collected in the Department of Pringles, San Luis, Argentina, in December 1994 and December 2001. A voucher specimen was deposited at Museo Botánico, Universidad Nacional de Córdoba, under No. CORD 8039.

Seed Germination Bioassays. Seeds of *Lactuca sativa* L. and *Zea mays* L. were obtained from Instituto Nacional de Tecnología Agropecuaria (INTA, Córdoba, Argentina). *Sorghum halepense* L., *Chenopodium album*, and *Ipomea purpurea* were obtained from Laboratorio de Semillas (Facultad de Ciencias Agropecuarias, UNC, Argentina). Bioassays were carried out as reported previously.[11] Germination and root length values of treated and control experiments were analyzed by ANOVA test ($p < 0.05$).

Extraction and Isolation. The air-dried powdered aerial parts of *J. bergii* (500 g) were extracted exhaustively with EtOH, and the EtOH extract was concentrated at reduced pressure. The residue (60.03 g) was defatted by partition in hexane−MeOH−H_2O (10:9:1), the MeOH−H_2O phase was washed with hexane (3 × 200 mL), and the MeOH was evaporated at reduced pressure. The residue was diluted with H_2O and extracted with CH_2Cl_2 (3 × 200 mL). The CH_2Cl_2 extract was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness at reduced pressure. The residue from the plant collected in 1994 (5 g) was chromatographed on Kieselgel 60-G. Elution with CH_2Cl_2−MeOH mixtures of increasing polarity (100:0−90:10) afforded two fractions containing withanolides. The fraction eluting with 98:2 CH_2Cl_2−MeOH was subjected to column chromatography with 8:2 ethyl acetate−hexane, yielding **1** (50 mg). The fraction eluting with 95:5 CH_2Cl_2−MeOH was subjected to column chromatography with 9:1 ethyl acetate−hexane to give a mixture that was further fractionated by preparative reversed-phase TLC (water−acetonitrile, 1:1), yielding compounds **5** (10 mg) and **4** (5 mg). The residue from the plant collected in 2001 (3.7 g) was chromatographed in Kieselgel 60-G. Elution with ethyl acetate−hexane mixtures of increasing polarity gave two fractions containing withanolides. The fraction eluting with 8:2 ethyl acetate−hexane was further fractionated by radial chromatography on silica gel, eluting with CH_2Cl_2−MeOH mixtures of increasing polarity (99.5:0.5 to 95:5). This led to the isolation of (in order of elution) **2** (10 mg), **7** (16 mg), **1** (10 mg), and **6** (7 mg). From the fraction eluting with 9:1 ethyl acetate−hexane, compound **3** (32 mg) precipitated.

Jaborosalactol 18 ((15*S*,17*R*,20*R*,22*R*,24*S*,25*S*,26*R*)-5*β*,6*β*:22,26:24,25-triepoxy-14α,17,26-trihydroxy-15,21-cycloergost-2-en-1-one, 1): colorless crystals (hexane−EtOAc), mp 214−216 °C; $[\alpha]^{21}_D$ +30.6° (*c* 0.001, $CHCl_3$); UV (MeOH) λ_{max} 222 nm; IR (dry film) ν_{max} 3470, 1673, 1479, 1031 cm^{-1}; ^{1}H NMR (500.13 MHz), see Table 1; ^{13}C NMR (125.77 MHz), see Table 2; EIMS *m*/*z* 450 (M − $2H_2O$, 2), 432 (450 − H_2O, 2), 377 (1), 243 (2), 225 (6), 153 (5), 143 (4), 135 (11), 127 (7), 122 (97), 109 (30), 43 (100); HRCIMS (isobutane) *m*/*z* 487.2709 $[M + H]^+$ (calcd for $C_{28}H_{39}O_7$, 487.2696).

Jaborosalactol 19 ((15*S*,17*R*,20*R*,22*R*,24*S*,25*S*,26*R*)-5*β*,6*β*:22,26:24,25-triepoxy-17,26-dihydroxy-15,21-cycloergosta-2,8(14)-dien-1-one, 2): white amorphous powder (hexane−EtOAc), mp 148 °C (dec); $[\alpha]^{21}_D$ +89.2° (*c* 0.0045 $CHCl_3$); UV (MeOH) λ_{max} 215 nm; IR (dry film) ν_{max} 3287, 1673, 1469, 1036 cm^{-1}; ^{1}H NMR (500.13 MHz), see Table 1; ^{13}C NMR (50.32 MHz), see Table 2; EIMS, 468 $[M]^+$ (10), 450 (40), 420 (18), 377 (48), 307 (9), 225 (32), 143 (26), 127 (9), 122 (43), 109 (100); HREIMS *m*/*z* 468.2513 (calcd for $C_{28}H_{36}O_6$, 468.2512).

Jaborosalactol 20 ((15*S*,17*R*,20*R*,22*R*,24*S*,25*S*,26*R*)-22,-26:24,25-diepoxy-5α,6*β*,17,26-tetrahydroxy-15,21-cycloergosta-2,8(14)-dien-1-one, 3): colorless crystals (hexane−EtOAc), mp 220−222 °C; $[\alpha]^{21}_D$ +90.7° (*c* 0.0035 $CHCl_3$); UV (MeOH) λ_{max} 220 nm; IR (dry film) ν_{max} 3220, 1673, 1087 cm^{-1}; ^{1}H NMR (200.13 MHz), see Table 1; ^{13}C NMR (50.32 MHz), see Table 2; EIMS *m*/*z* 486 $[M]^+$ (5), 468 (58), 451 (7), 450 (21), 438 (48), 423 (12), 395 (26), 368 (8), 328 (6), 315 (9), 143 (13), 127 (5), 122 (50), 109 (100); HREIMS *m*/*z* 486.2625 (calcd for $C_{28}H_{38}O_7$, 486.2618).

Jaborosalactol 21 ((15*S*,17*R*,20*R*,22*R*,24*S*,25*S*,26*R*)-5α-chloro-22,26:24,25-diepoxy-6*β*,17,26-trihydroxy-15,21-cycloergosta-2,8(14)-dien-1-one, 4): colorless crystals (hexane−acetone), mp 183−185 °C (dec); IR (dry film) ν_{max} 3420, 1693, 1561, 1545, 1515, 1378, 1016, 863 cm^{-1}; ^{1}H NMR (500.13 MHz), see Table 1; ^{13}C NMR (125.77 MHz), see Table 2; EIMS *m*/*z* 450 (M − HCl − H_2O, 1), 413 (1), 377 (2), 143 (3), 109 (15), 43 (100).

Jaborosalactol 23 ((17*R*,20*R*,22*R*,24*S*,25*S*,26*R*)-5α-chloro-22,26:24,25-diepoxy-6*β*,14*β*,17,26-tetrahydroxyergost-2-en-1-one, 6): colorless crystals (hexane−EtOAc), mp 173 °C (dec); $[\alpha]^{21}_D$ +13.2° (*c* 0.004 $CHCl_3$); UV (MeOH) λ_{max} 225 nm; IR (dry film) ν_{max} 3220, 1683, 1469, 1036 cm^{-1}; ^{1}H NMR (500.13 MHz), see Table 1; ^{13}C NMR (50.32 MHz), see Table 2; EIMS *m*/*z* 452 (M − HCl − $2H_2O$, 10), 346 (15), 310 (15), 143 (18), 127 (13), 124 (100), 121 (31), 109 (98); HRFABMS *m*/*z* 547.2423 $[M + Na]^+$ (calcd for $C_{28}H_{41}O_7ClNa$ 547.2439).

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Supporting Information Available: AM1 calculated structure of jaborosalactone 18 (**1**) and relevant NOEs observed. This information is available free of charge via the Internet at http://pubs.acs.org

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