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TRITERPENE GLYCOSIDES FROM *Astragalus* AND THEIR GENINS. LXXVIII. CHEMICAL TRANSFORMATION OF CYCLOARTANES. VI. PARTIAL SYNTHESIS OF CYCLOADSURGENIN[a]

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*Cycloadsurgenin, 20*R,*24*S*-epoxycycloartan-6α,25-diol-3,16-dione, was partially synthesized in four steps from cyclosieversigenin. Side products with the structures 17*E*,24*S*-cycloart-17-en-6α,24,25-triol-3,16-dione and 17*Z*,24*S*-cycloart-17-en-6α,24,25-triol-3,16-dione were obtained in addition to the desired product.*

Key words: *Astragalus*, Leguminosae, cycloartanes, cycloadsurgenin, PMR and ^{13}C NMR spectra, DEPT.

In continuation of the chemical transformation of cycloartanes [1], cycloadsurgenin (**8**) was partially synthesized in four steps from cyclosieversigenin (**1**). Cycloadsurgenin is a natural cycloartane triterpenoid that is isolated from *Astragalus adsurgens* Pall. (Leguminosae) [2] and has the structure 20*R*,24*S*-epoxycycloartan-6α,25-diol-3,16-dione, i.e., the 3,16-diketone of cyclosieversigenin. Therefore, the chemical structures of these triterpenoids were correlated by synthesizing cycloadsurgenin from cyclosieversigenin, which was prepared by acid hydrolysis of the total glycosides isolated from *A. sieversianus* Pall. [3].

Cyclosieversigenin was acetylated by acetic anhydride in pyridine under the conditions described in the Experimental section to give primarily one product that was purified by column chromatography and identified with the previously reported 3,6-diacetate of cyclosieversigenin (**2**) [4]. This product was saponified by methanolic $KHCO_3$ at room temperature. The reaction products included **3** and **4** and a small amount of cyclosieversigenin. The PMR (see Experimental) and ^{13}C (Table 1) NMR spectra showed that **3** and **4** were monoacetates that gave quasi-molecular ions in electrospray positive-ion and negative-ion mass spectra (MS ES PI and MS ES NI) with *m*/*z* 555.4 $[M + Na]^+$ and 531.2 $[M - H]^-$. IR spectra of **3** and **4** that exhibited absorption bands for esters were consistent with this.

The PMR spectrum of **3** contained a 3H singlet at δ 1.99. The resonance for H-3 in this same spectrum underwent a weak-field shift compared with that for cyclosieversigenin and appeared at δ 4.50 as a doublet of doublets with SSCC $^3J_1 = 11$ and $^3J_2 = 4.7$ Hz. In correspondence with this, the ^{13}C NMR spectrum of **3** showed resonances for a single acetyl group at δ 171.29 and 21.83 and a resonance for C-3 at δ 80.57. These data defined **3** as the 3-monoacetate of cyclosieversigenin.

The PMR spectrum of the other product **4** also contained a 3H singlet at δ 1.95. The resonance for H-6 in this same spectrum was observed at δ 4.70 as a triplet of doublets with SSCC $^3J_1 = {}^3J_2 = 9.1$ and $^3J_3 = 4.5$ Hz. These values were practically the same as those for the 3,6-diacetate of cyclosieversigenin (**2**) and indicated that **4** retained the C-6 acetyl. This was also evident in the ^{13}C NMR spectrum of **4**, where C-6 resonated at δ 71.14 whereas the resonance for C-3 underwent a strong-field shift and was observed at δ 78.23. Therefore, **4** was the 6-monoacetate of cyclosieversigenin.

Monoacetate **4** was oxidized by Jones reagent [5]. Separation of the oxidation products over a column produced ketones **5**-**7**. The PMR and ^{13}C NMR spectra of **5**-**7** showed that the side chain of these compounds had not changed, i.e., the cycloartane carbon skeleton was preserved. The ^{13}C NMR spectrum of **5** exhibited two resonances for ketone C atoms at δ 215.66 and 217.71. In agreement with this, the PMR spectrum of **5** lacked resonances for H-3 and H-16 and the resonance for H-17 was transformed into a singlet at δ 2.84. These data defined **5** as 6-acetoxy-20*R*,24*S*-epoxycycloartan-25-ol-3,16-dione. This agreed completely with the IR and mass spectra.

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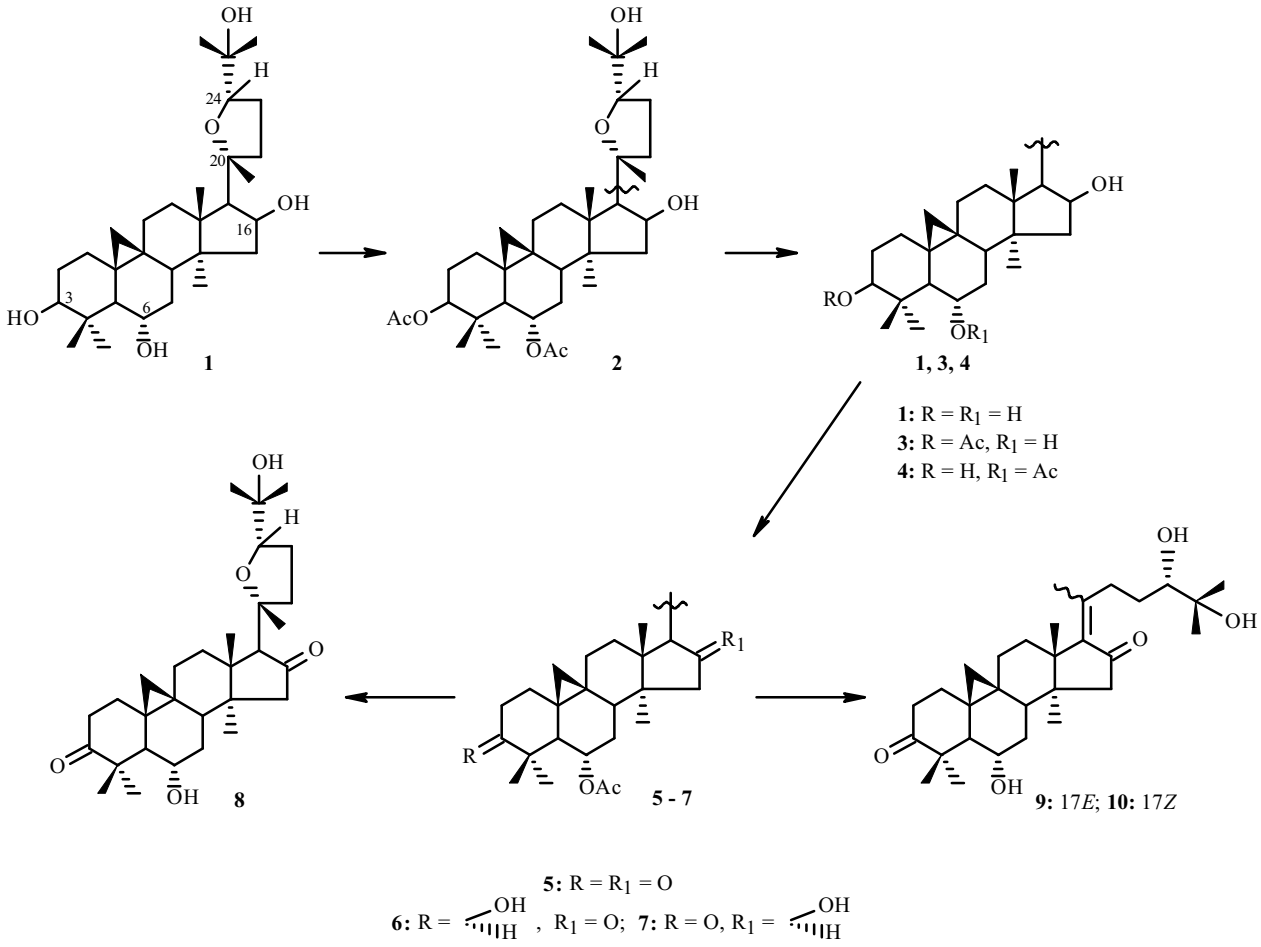


The ^{13}C NMR spectrum of oxidation product **6** had one resonance for a ketone carbonyl at δ 218.24. The PMR spectrum of this product clearly showed the H-3 resonance as a doublet of doublets at δ 3.26 with SSCC $^3J_1 = 11$ and $^3J_2 = 4.5$ Hz and the H-17 resonance as a singlet at δ 2.84. As expected, the resonance of H-16 was absent. In agreement with this, the IR spectrum of **6** contained an absorption band at 1730 cm^{-1} that was characteristic of a five-membered cyclic ketone. Quasi-molecular ions with *m/z* 553.3 $[M + Na]^+$ and 529.1 $[M - H]^-$ in mass spectra of this compound also confirmed that **6** was a monoketone. These results defined it as 6-acetoxy-20*R*,24*S*-epoxycycloartan-3*β*,25-diol-16-one.

The ^{13}C NMR spectrum of the third oxidation product **7** also exhibited a resonance for a single ketone carbonyl at δ 216.19. The PMR spectrum of **7** showed the H-16 resonance at δ 4.62 as a triplet of doublets with SSCC $^3J_1 = {}^3J_2 = 7.9$ and $^3J_3 = 6.3$ Hz and the H-17 resonance at δ 2.27 as a doublet with SSCC $^3J = 7.9$ Hz. The resonance for H-3 was absent. The IR spectrum of **7** exhibited an absorption band for a six-membered cyclic ketone at 1702 cm^{-1} that was consistent with this. Quasimolecular ions with *m/z* 553.4 $[M + Na]^+$ and 531.4 $[M + H]^+$ in the mass spectrum of **7** also indicated that this compound was a monoketone. Therefore, **7** had the structure 6-acetoxy-20*R*,24*S*-epoxycycloartan-16*β*,25-diol-3-one.

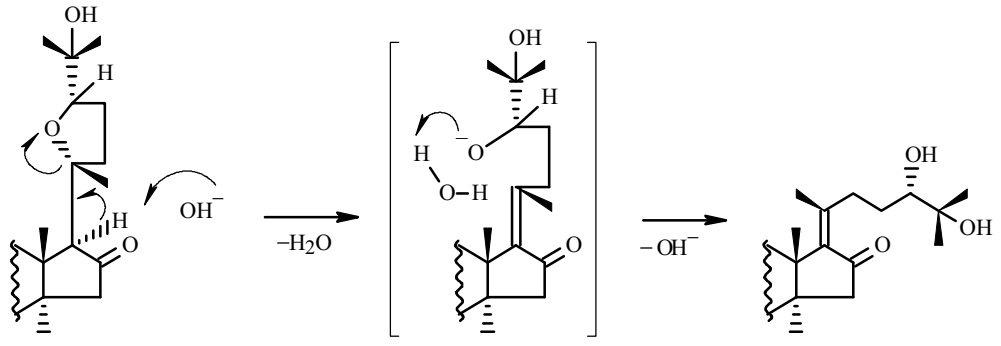
Alkaline hydrolysis of **5** produced **8**-**10**. Column chromatography of the reaction products isolated pure diketone **8**, a fraction containing diketones **9** and **10**, and pure diketone **10**. The PMR and ^{13}C NMR spectra and the IR and mass spectra of **8** defined it as cycloadsurgenin [2].

TABLE 1. Chemical Shifts of C Atoms of **1-8** and **10** ($CDCl_3$, δ, ppm, 0 = HMDS)

C atom	Compound								
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**10**
1	32.45	31.78	32.10	32.15	31.97	32.05	32.20	31.55	31.90
2	31.80	25.93	27.13	30.54	36.07	30.47	36.28	35.29	35.79
3	78.70	79.97	80.57	78.23	215.66	78.10	216.19	217.32	217.17
4	41.85	40.49	40.74	41.59	50.29	41.63	50.35	50.16	50.51
5	53.98	50.10	54.13	50.03	50.47	49.97	50.63	52.99	53.74
6	69.43	70.71	69.19	71.14	71.59	70.71	71.93	69.22	69.74
7	38.30	33.28	38.34	33.48	32.07	33.63[a]	33.53	37.66	37.67
8	47.47	45.15	47.56	45.35	45.94	44.58	46.59[a]	46.99	45.76
9	21.07	21.01	21.11	20.89	21.00[a]	20.56	21.43	20.40	20.89
10	29.82	28.57	29.70	28.82	28.59	29.08	28.35	28.50	28.70
11	26.02	26.18	26.05	25.96	26.09	25.98	25.91	25.69	26.13
12	33.35	33.31	33.26	33.33	33.63[b]	33.63[a]	33.22	31.36[a]	32.60
13	45.35	45.41	45.30	45.39	44.92	44.96	45.41	44.34	48.30
14	46.35	46.27	46.31	46.27	42.47	42.51	46.30	42.00	42.27
15	46.87	46.18	46.88	46.21	51.39	51.10	46.59[a]	51.44	51.54
16	73.72	73.64	73.69	73.67	217.71	218.24	73.62	218.54	208.97
17	57.87	57.67	57.82	57.70	65.69	65.53	57.86	65.20	152.55
18	21.82	21.25	21.66	21.33	21.00[a]	19.73	21.87	20.48	21.41[a]
19	30.63	29.39	31.88	29.61	30.57	29.58	30.51	31.24	30.60
20	87.42	87.40	87.39	87.43	84.74	84.82	87.36	84.41	141.33
21	28.03	28.06	28.03	28.06	26.72	25.56	28.07	25.16	24.08
22	34.79	34.75	34.77	34.73	33.63[b]	32.13	34.77	31.36[a]	31.29
23	26.22	26.93	26.23	26.17	26.64	26.65	26.26	26.32	31.12
24	81.76	81.71	81.72	81.69	82.57	82.49	81.74	81.91	77.49
25	72.13	72.10	72.14	72.12	71.03	71.07	72.14	71.03	72.69
26	26.80	26.85	26.81	26.89	25.58	25.46	26.88	28.00	23.98
27	28.16	26.83	28.20	26.95	25.41	26.94	26.57	25.12	26.40
28	20.40	20.08	20.41	20.10	20.01	20.00	20.39	19.86*	20.42
29	28.54	28.12	28.49	28.14	28.37	28.36	28.07	28.12	28.17
30	15.62	16.59	16.69	15.48	20.57	15.47	21.08	19.84*	21.41[a]
C-3-Ac	-	171.22	171.29	-	-	-	-	-	-
	-	21.60	21.83	-	-	-	-	-	-
C-6-Ac	-	170.73	-	170.78	170.53	170.75	170.55	-	-
	-	22.17	-	22.23	21.98	22.16	22.06	-	-

Resonances marked with the same letters are overlapped within columns; *ambiguous assignment.

The ^{13}C NMR spectrum of **10** exhibited resonances for two ketone carbonyls at δ 208.97 and 217.17 and two C atoms of a tetra-substituted olefin at δ 141.33 and 152.55. The PMR spectrum of **10** lacked a resonance for H-17 whereas a single methyl group resonated at δ 1.86. This indicated that the methyl was bonded to an olefinic C atom and that the double bond in **10** was located at C-17—C-20. Therefore, the tetrahydrofuran ring was opened by the following mechanism:



The spectrum of ketone **9** was obtained by subtracting the PMR spectrum of **10** from that of a mixture of ketones **9** and **10**. The PMR spectrum of **9** and **10** indicated that these compounds were geometric isomers, i.e., isomers differing in the configuration of the substituents on olefinic C atom C-20.

The methyl CH_3-21 resonated in the PMR spectrum of **9** at δ 2.12. The same methyl was observed in the PMR spectrum of **10** at δ 1.87 (1.86). Therefore, methyl CH_3-21 and the C-16 carbonyl in **9** were located on the same side of the double bond, i.e., ketone **9** had the 17*E*-configuration.

Thus, **9** was 17*E*,24*S*-cycloart-17-en-6α,24,25-triol-3,16-dione; **10**, 17*Z*,24*S*-cycloart-17-en-6α,24,25-triol-3,16-dione.

EXPERIMENTAL

General comments have been published [6]. We used solvent systems $CHCl_3$:CHOH (20:1, 1; 50:1, 2; 90:1, 3).

PMR and ^{13}C NMR spectra in $CDCl_3$ were obtained on a UNITYplus 400 spectrometer with HMDS internal standard with the exception of **8**, the spectrum of which was recorded in $CDCl_3$ on an INOVA 600 spectrometer (Varian) with TMS internal standard. ^{13}C NMR spectra were recorded with full C–H decoupling and DEPT; IR spectra in KBr disks, on a Bio-Rad FT-IR Spectrometer 165.

Electrospray positive- and negative-ion mass spectra (MS ES PI and MS ES NI) were obtained on a Waters Alliance 2690-ZQ4000 (LC/MS) spectrometer.

Methanolysis of Compounds Extracted from Roots of *A. sieversianus* Pall. Dry extract of roots of *A. sieversianus* (100 g) that was prepared as before [3] was dissolved in methanolic H_2SO_4 (1 L, 0.25%), refluxed on a water bath for 48 h, evaporated to a small volume (0.5 L), diluted with water (1 L), and evaporated to remove methanol. The aqueous solution was extracted with ethylacetate. The ethylacetate extract was washed with water and evaported to dryness. The residue was chromatographed over a silica-gel column with elution successively by $CHCl_3$ and system 1 to afford **1** (4 g), mp 239-241°C (methanol).

PMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.31 and 0.45 (2H-19, d, $^2J = 4.5$), 0.89, 0.90, 1.08, 1.16, 1.20, 1.20, 1.23 (7 × CH_3, s), 2.27 (H-17, d, $^3J = 7.9$), 2.51 (H-22, q, $^3J_1 = {}^3J_2 = {}^2J = 11.6$), 3.24 (H-3, dd, $^3J_1 = 11$, $^3J_2 = 4.5$), 3.47 (H-6, td, $^3J_1 = {}^3J_2 = 9.9$, $^3J_3 = 3.4$), 3.68 (H-24, t, $^3J_1 = {}^3J_2 = 7.9$), 4.62 (H-16, td, $^3J_1 = {}^3J_2 = 7.9$, $^3J_3 = 6.3$). Table 1 gives the ^{13}C NMR spectrum.

3,6-Diacetate of Cyclosieversigenin (2) from 1. Cyclosieversigenin (**1**, 1 g) was acetylated by acetic anhydride (2.5 mL) in anhydrous pyridine (5 mL) over 6.5 h at 17°C. The mixture was poured onto ice. The resulting precipitate was filtered off. The product was separated over a column with elution by solvent system 2 to afford **2** (1.098 g), $C_{34}H_{54}O_7$, mp 211-212°C (methanol) [4].

PMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.29 and 0.55 (2H-19, d, $^2J = 4.8$), 0.78, 0.89, 0.93, 1.09, 1.16, 1.18, 1.24 (7 × CH_3, s), 1.70 (H-5, d, $^3J = 9.7$), 1.93 (CH_3COO on C-6, s), 1.99 (CH_3COO on C-3, s), 2.27 (H-17, d, $^3J = 7.9$), 2.51 (H-22, q, $^2J = {}^3J_1 = {}^3J_2 = 10$), 3.69 (H-24, t, $^3J_1 = {}^3J_2 = 7.4$), 4.51 (H-3, dd, $^3J_1 = 11$, $^3J_2 = 4.6$), 4.62 (H-16, td, $^3J_1 = {}^3J_2 = 7.9$, $^3J_3 = 6.3$), 4.69 (H-6, td, $^3J_1 = {}^3J_2 = 9.2$, $^3J_3 = 4.5$). Table 1 gives the ^{13}C NMR spectrum.

Cyclosieversigenin (1), Cyclosieversigenin 3-Monoacetate (3), and Cyclosieversigenin 6-Monoacetate (4) from 2. A solution of cyclosieversigenin (**2**, 1.095 g) in methanol (35 mL) was treated with $KHCO_3$ (150 mg) in the same solvent (15 mL) and left for 14 d at 50°C. The mixture was poured into water. The products were extracted by $CHCl_3$. The usual workup and evaporation of $CHCl_3$ gave a solid that was chromatographed over a column using solvent system 2 to afford starting diacetate **2** (158 mg). Further elution of the column by the same solvent system gave amorphous cyclosieversigenin 6-monoacetate (**4**, 604 mg), $C_{32}H_{54}O_6$.

IR spectrum (KBr, ν, cm^{-1}): 3417 (OH), 1734, 1247 (ester).

MS ES PI (*m*/*z*): $[M + Na]^+$ 555.4. MS ES NI (*m*/*z*): $[M - H]^-$ 531.2.

PMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.28 and 0.53 (2H-19, d, $^2J = 4.6$), 0.85, 0.88, 0.92, 1.09, 1.16, 1.18, 1.24 (7 × CH_3, s), 1.95 (CH_3COO, s), 2.26 (H-17, d, $^3J = 7.7$), 2.51 (H-22, q, $^3J_1 = {}^3J_2 = {}^2J = 10.6$), 3.23 (H-3, dd, $^3J_1 = 11$, $^3J_2 = 4.7$), 3.69 (H-24, t, $^3J_1 = {}^3J_2 = 7.3$), 4.62 (H-16, td, $^3J_1 = {}^3J_2 = 7.9$, $^3J_3 = 6.3$), 4.70 (H-6, td, $^3J_1 = {}^3J_2 = 9.1$, $^3J_3 = 4.5$). Table 1 gives the ^{13}C NMR spectrum.

Further elution of the column with the same solvent system isolated **3** (130 mg), $C_{32}H_{52}O_6$, mp 243-245°C (methanol).

IR spectrum (KBr, ν, cm^{-1}): 3396 (OH), 1735, 1251 (ester).

MS ES PI (*m/z*): $[M + Na]^+$ 555.4. MS ES NI (*m/z*): $[M - H]^-$ 531.2.

PMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.32 and 0.47 (2H-19, d, $^2J = 4.4$), 0.89, 0.98, 1.06, 1.07, 1.15, 1.19, 1.23 (7 × CH_3, s), 1.99 (CH_3COO, s), 2.27 (H-17, d, $^3J = 7.6$), 2.52 (H-22, q, $^3J_1 = {}^3J_2 = {}^2J = 10$), 3.45 (H-6, td, $^3J_1 = {}^3J_2 = 9.7$, $^3J_3 = 3.2$), 3.68 (H-24, t, $^3J_1 = {}^3J_2 = 7.5$), 4.50 (H-3, dd, $^3J_1 = 11$, $^3J_2 = 4.7$), 4.62 (H-16, q, $^3J_1 = {}^3J_2 = {}^3J_3 = 7.5$). Table 1 gives the ^{13}C NMR spectrum.

Further elution of the column by system 1 gave **1** (4 mg).

6-Acetoxy-20*R*,24*S*-epoxycycloartan-25-ol-3,16-dione (5), 6-Acetoxy-20*R*,24*S*-epoxycycloartan-3β,25-diol-16-one (6), and 6-Acetoxy-20*R*,24*S*-epoxycycloartan-16β,25-diol-3-one (7) from 4. Monoacetate **4** (550 mg) in acetone (100 mL) at −8°C was treated with Jones reagent (0.5 mL) [5] and stirred for 35 min. The excess of oxidant was destroyed by adding several milliliters of methanol to the mixture. The solution was poured into water. The products were extracted with $CHCl_3$. The usual workup and evaporation of $CHCl_3$ followed by separation over a column with elution by system 3 isolated **5** (128 mg), $C_{32}H_{48}O_6$, mp 126-128°C (methanol).

IR spectrum (KBr, ν, cm^{-1}): 3432 (OH), 1737 (>C=O on C-16), 1706 (>C=O on C-3), 1737, 1243 (ester).

MS ES PI (*m/z*): $[M + Na]^+$ 551.3. MS ES NI (*m/z*): $[M - H]^-$ 527.1.

PMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.50 and 0.73 (2H-19, d, $^2J = 4.7$), 1.04, 1.08, 1.08, 1.11, 1.14, 1.15, 1.19 (7 × CH_3, s), 1.97 (CH_3COO, s), 2.19 (H-5, d, $^3J = 10$), 2.84 (H-17, s), 3.67 (H-24, dd, $^3J_1 = 8.3$, $^3J_2 = 6$), 4.66 (H-6, td, $^3J_1 = {}^3J_2 = 10$, $^3J_3 = 3.7$). Table 1 gives the ^{13}C NMR spectrum.

Further elution of the column by the same solvent system isolated **6** (41 mg), $C_{32}H_{50}O_6$, mp 133-135°C (system 3), solidifying at 145-150°C, melting at 175-177°C.

IR spectrum (KBr, ν, cm^{-1}): 3449 (OH), 3047 (cycloartane CH_2), 1730 (>C=O on C-16), 1730, 1248 (ester).

MS ES PI (*m/z*): $[M + Na]^+$ 553.3. MS ES NI (*m/z*): $[M - H]^-$ 529.1.

PMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.35 and 0.56 (2H-19, d, $^2J = 4.8$), 0.86, 0.93, 1.04 (3 × CH_3, s), 1.07 (CH_3-28, d, $^4J = 0.8$), 1.12, 1.13, 1.19 (3 × CH_3, s), 1.65 (H-5, d, $^3J = 9.9$), 1.94 (CH_3COO, s), 2.06 (H-15β, dq, $^2J = 18$, $^4J = 0.8$), 2.84 (H-17, s), 3.26 (H-3, dd, $^3J_1 = 11$, $^3J_2 = 4.5$), 3.67 (H-24, dd, $^3J_1 = 8.3$, $^3J_2 = 5.8$), 4.69 (H-6, td, $^3J_1 = {}^3J_2 = 9$, $^3J_3 = 4.3$). Table 1 gives the ^{13}C NMR spectrum.

Further elution of the column with the same system gave monoketone **7** (135 mg), $C_{32}H_{50}O_6$, mp 111-114°C (system 3).

IR spectrum (KBr, ν, cm^{-1}): 3424 (OH), 1734, 1245 (ester), 1702 (>C=O on C-3).

MS ES PI (*m/z*): $[M + Na]^+$ 553.4. MS ES NI (*m/z*): $[M - H]^-$ 531.4.

PMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.43 and 0.71 (2H-19, d, $^2J = 4.5$), 0.89, 1.08, 1.09, 1.10, 1.17, 1.22, 1.25 (7 × CH_3, s), 1.97 (CH_3COO, s), 2.14 (H-5, d, $^3J = 10$), 2.27 (H-17, d, $^3J = 7.9$), 2.50 (2H-2, 1H-22, m), 3.70 (H-24, t, $^3J_1 = {}^3J_2 = 7.2$), 4.62 (H-16, td, $^3J_1 = {}^3J_2 = 7.9$, $^3J_3 = 6.3$), 4.68 (H-6, td, $^3J_1 = {}^3J_2 = 10$, $^3J_3 = 3.6$). Table 1 gives the ^{13}C NMR spectrum.

Cycloadsurgenin (8), 17*E*,24*S*-Cycloart-17-en-6α,24,25-triol-3,16-dione (9), and 17*Z*,24*S*-Cycloart-17-en-6α,24,25-triol-3,16-dione (10) from 5. Monoacetate **5** (50 mg) was hydrolyzed by methanolic NaOH (10 mL, 0.1%) for 2 d at room temperature. The mixture was poured into water and treated with ethylacetate. The ethylacetate extract was washed with water and evaporated. The solid was chromatographed over a column with elution by system 2 to isolate **8** (15 mg), $C_{30}H_{46}O_5$, mp 243-247°C ($CHCl_3$:CH_3OH, 1:1).

IR spectrum (KBr, ν, cm^{-1}): 3410, 3367 (OH), 1726 (>C=O on C-16), 1702 (>C=O on C-3).

MS ES PI (*m/z*): $[M + Na]^+$ 509.3. MS ES NI (*m/z*): $[M - H]^-$ 485.1.

PMR spectrum (600 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.45 and 0.66 (2H-19, d, $^2J = 4.2$), 1.08, 1.15, 1.16, 1.17, 1.20, 1.23, 1.37 (7 × CH_3, s), 2.92 (H-17, s), 3.50 (H-6, td, $^3J_1 = {}^3J_2 = 9.6$, $^3J_3 = 4.8$), 3.71 (H-24, dd, $^3J_1 = 8.4$, $^3J_2 = 6$). Table 1 gives the ^{13}C NMR spectrum.

Further elution of the column with the same solvent system produced **9** and **10** (5 mg of the mixture, 0.6:1 according to the integrated intensities in the PMR spectrum).

PMR spectrum of **9** (400 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.43 and 0.64 (2H-19, d, $^2J = 4$), 0.978 (CH_3-28, d, $^4J = 1.3$), 1.09, 1.12, 1.18, 1.300, 1.305 (5 × CH_3, s), 2.12 (CH_3-21, s), 3.28 (H-24, dd, $^3J_1 = 10.6$, $^3J_2 = 1.9$), 3.51 (H-6, td, $^3J_1 = {}^3J_2 = 10.8$, $^3J_3 = 3.2$).

PMR spectrum of **10** (400 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.44 and 0.65 (2H-19, d, $^2J = 4$), 0.984 (CH_3-28, d, $^4J = 1.2$), 1.09, 1.12, 1.17, 1.299, 1.310 (5 × CH_3, s), 1.87 (CH_3-21, s), 3.21 (H-24, dd, $^3J_1 = 10.7$, $^3J_2 = 1.6$), 3.51 (H-6, td, $^3J_1 = {}^3J_2 = 10.8$, $^3J_3 = 3.2$).

Further elution of the column by the same solvent system isolated **10** (4.5 mg), $C_{30}H_{46}O_5$.

IR spectrum (KBr, ν, cm^{-1}): 3422 (OH), 1699 (>C=O on C-3 and C-16).

MS ES PI (*m*/*z*): $[M + Na]^+$ 509.3. MS ES NI (*m*/*z*): $[M - H]^-$ 485.1.

PMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz, 0 = HMDS): 0.44 and 0.64 (2H-19, d, $^2J = 4.5$), 0.975 (CH_3-28, d, $^4J = 1.2$), 1.08, 1.11, 1.16, 1.29, 1.30 (5 × CH_3, s), 1.77 (H-8, dd, $^3J_1 = 12$, $^3J_2 = 4.5$), 1.86 (CH_3-21, s), 1.92 (H-5, d, $^3J = 9.6$), 2.00 (H-15α, d, $^2J = 16.8$), 2.22 (H-15β, dq, $^2J = 16.8$, $^4J = 1.2$), 3.21 (H-24, dd, $^3J_1 = 10.7$, $^3J_2 = 1.3$), 3.51 (H-6, td, $^3J_1 = {}^3J_2 = 10$, $^3J_3 = 3.5$). Table 1 gives the ^{13}C NMR spectrum.

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