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# *Astragalus* TRITERPENE GLYCOSIDES AND THEIR GENINS. I. STRUCTURES OF CYCLOALPIGENIN AND CYCLOALPIOSIDE

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*Another two methylsteroids of the cycloartane series have been isolated from the epigeal part of* Astragalus alopecurus. *The structures of the compounds isolated, cycloalpigenin and cycloalpioside, have been established as (20R,24R)-16β,24:20,24-diepoxycycloartane-3β,7β,25-triol and (20R,24R)-16β,24:20,24-diepoxycycloartane-3β,7β,25-triol 3-O-β-D-xylopyranoside, respectively, on the basis of chemical transformations and spectral characteristics. The structure of cycloalpigenin has been confirmed by chemical correlation with that of cycloalpigenin D.*

We have previously isolated eight cycloartane methylsteroids from *Astragalus alopecurus* Pall. and have established their structures [1-4]. On analyzing intermediate fractions, we have detected and isolated another two components which we have called cycloalpigenin (**1**) and cycloalpioside (**10**). The present work was devoted to determining the structures of these compounds.

In the $^1$H NMR spectrum of the new genin (**1**) we traced two one-proton doublets of an *AB* system at 0.29 and 0.79 ppm with a characteristic SSCC $^2J$ = 4 Hz, relating to an isolated cyclopropane methylene, and also the singlet signals of seven methyl groups in the high field (Table 1). In agreement with this, in the $^{13}$C NMR spectrum of the compound under study (Table 2), we observed at 19.48, 27.66, and 30.14 ppm the resonance lines of two quaternary and one secondary carbon atoms forming a 1,1,2,2-tetrasubstituted cyclopropane system representing the 9,19-three-membered ring of a cycloartane. The facts given and the elementary composition, $C_{30}H_{48}O_5$ enabled us unambiguously to assign compound (**1**) to the triterpenoids of the cycloartane series [5, 6].

The IR spectrum of cycloalpigenin had a broad absorption band of hydroxy groups. When the $^1$H and $^{13}$C NMR spectra, showing the absence of $sp^2$ hybridization, were also taken into account, it followed from the elementary composition of the compound under consideration, $C_{30}H_{48}O_5$, that only three of the oxygen atoms are in the form of hydroxy groups, while the other two must form epoxide rings. The presence of the singlet signal of an anomeric proton at 110.60 ppm in the $^{13}$C NMR spectrum of genin (**1**) showed that the epoxide rings form a ketal system.

The mass spectrum of cycloalpigenin contained the maximum peak of an ion a with *m/z* 143 ($C_8H_{15}O_2$), as in the spectra of 20,24-epoxycycloartan-25-ols. However, the $^1$H NMR spectrum of compound (**1**) lacked an H-24 signal. Consequently, C-24 is an anomeric carbon atom and one hydroxy group is present at C-25. This was also shown by the signal from a tertiary carbinol carbon atom in the $^{13}$C NMR spectrum at 72.83 ppm and by the peak of ion b with *m/z* 429 in the mass spectrum, arising on the cleavage of the C-24−C-25 bond with the the elimination of an isohydroxyisopropyl fragment.

The appearance of an ion with *m/z* 143 in the mass-spectrometric fragmentation of genin (**1**) presupposes the presence of a 20,24-epoxy function. This means that one of the epoxy functions links the ketalic carbon atom C-24 with the C-20 atom. The singlet nature of the signals of all the methyl groups in the $^1$H NMR spectrum of cycloalpigenin confirms this conclusion. Additional confirmation may be given by the C-20 signal, observed at 84.87 pp, in the $^{13}$C NMR spectrum of the compound under discussion.

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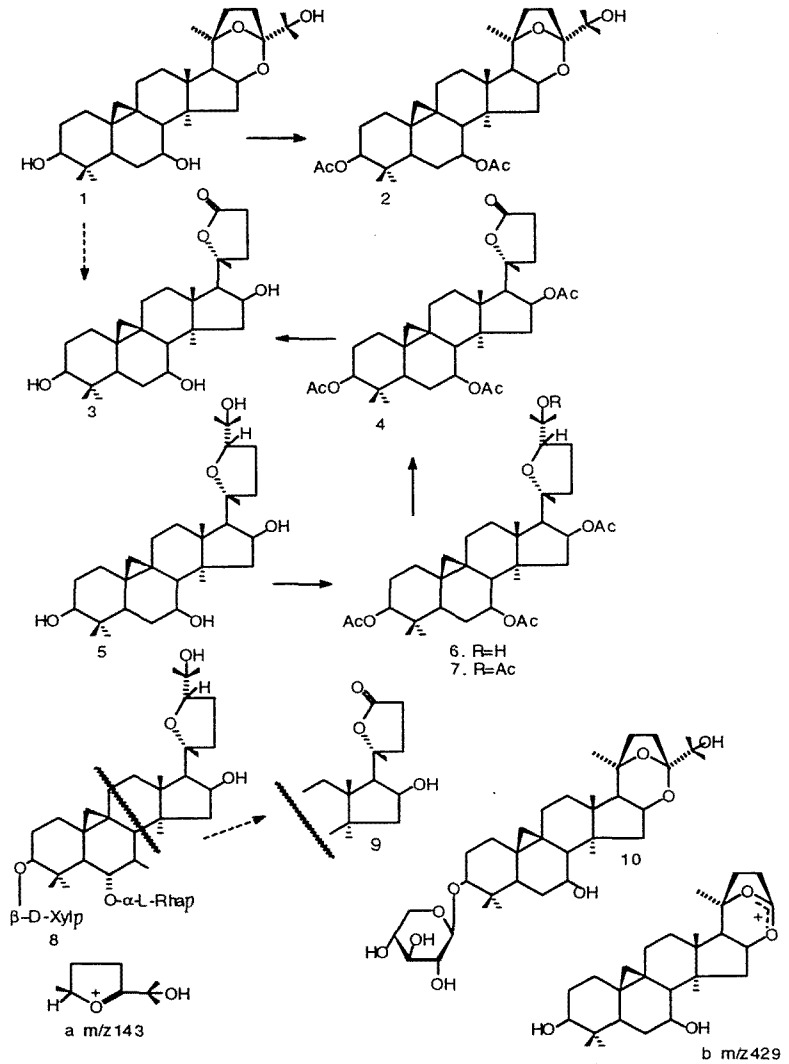


The doublet nature of the splitting of the H-17 signal at 2.64 ppm showed the presence of an oxygen function at C-16. In actual fact, the same $^1$H NMR spectrum contained a 1:3:3:1 quartet at 4.56 ppm with the SSCCs $^3J_1 = {}^3J_2 = {}^3J_3 =$ 8 Hz, relating to 16α−H. This signal underwent an upfield shift in comparison with the analogous signals of cycloartanes having a side-chain with a 20,24-epoxy-25-ol structure (**5**) [6]. This fact permitted the assumption that the second atom linked to the ketalic carbon atom through an epoxy function is C-16. As was to be expected, the C-16 signal suffered a downfield shift in comparison with that of cycloalpigenin D (**5**) and was observed at 74.38 ppm.

Thus, the side-chain of cycloalpigenin has a 16β,24:20,24-diepoxy-25-ol structure, and the two unidentified hydroxy groups are located in the polycyclic part of the molecule.

A consideration of the $^1$H and $^{13}$C NMR spectra of cycloalpigenin showed that both hydroxy groups are secondary. In agreement with this, the $^1$H NMR spectrum of genin (**1**) contained the signals of two protons geminal to hydroxy groups, at 3.53 ppm (dd, $^3J_1 = 10$, $^3J_2 = 4$ Hz) and 3.74 ppm (td, $^3J_1 = {}^3J_2 = 9$, $^3J_3 = 3$ Hz). In the spectrum of the diacetate (**2**), these signals had undergone a downfield shift and appeared at 4.50 and 4.72 ppm, respectively. The values of the chemical shift and the SSCCs of the doublet of doublets are characteristic for 3α−H, and, consequently, one of the missing hydroxy groups is present at C-3 and has the β- orientation [6]. The corresponding carbinol carbon atom resonated at 77.68 ppm and thereby confirmed the conclusion that cycloalpigenin molecule contains a 3β-hydroxy group.

The multiplicity of the H-3 signal showed the absence of an α-glycol grouping in the molecule. The triplet of doublets at 3.74 ppm therefore belongs to a proton located in ring *B*; namely, at C-6β or C-7α. Since the signal of the 4α-$CH_3$ group did not shift downfield to 1.8 ppm in the $^1$H NMR spectrum, the cycloalpigenin does not contain a 6α-hydroxy group [6]. This means that the hydroxy group present in ring *B* is located at C-7 and has the β-orientation [6]. This conclusion was confirmed by the chemical shift for C-7, 70.39 ppm [1, 7].

TABLE 1. Chemical Shifts ($\delta$, ppm), Multiplicities, and SSCCs (J, Hz) of the Protons of Cycloalpigenin (**1**), Cycloalpigenin D (**5**), and Their Derivatives (0 — TMS)

| Compound | Positions of the protons | | | | |
|---|---|---|---|---|---|
| | H-3 | H-7 | H-16 | 11-17 | 2H-19 |
| 1 | 3.53 dd (10; 4) | 3.74 td (9; 3) | 4.56 q (8; 8; 8) | 2.61 d (8) | 0.29; 0.79 d (4) |
| 2 | [4.50 dd (10; 4)] | [4.72 td (9; 3)] | [4.12 q (8; 8; 8)] | [2.40 d (8)] | [0.26; 0.72 d (4)] |
| 3 | 3.53 dd (10; 4) | 3.77 td (9;3) | 4.94 q (8; 8; 8) | 2.55 d (8) | 0.33; 0.78 d (4) |
| | [3.24 dd (10; 4)] | [3.48 td (11; 3)] | [4.55 q (8; 8; 8)] | [2.28 d (8)] | [0.31; 0.66 d (4)] |
| 4 | [4.25 dd (10; 4)] | [4.70 td (9; 3)] | [5.26 q (8; 8; 8)] | | [0.38; 0.68 d (4)] |
| 5 | 3.51 dd (10; 4) | 3.78 td (9; 3) | 5.06 q (8; 8; 8) | 2.50 d (8) | 0.29; 0.78 d (4) |
| 7 | 4.60 dd (11; 5) | 4.82 td (10; 4) | 5.44 td (7; 5) | | 0.22; 0.61 d (4) |

| Compound | Positions of the protons | | |
|---|---|---|---|
| | H-24 | $CH_3$ groups | OAc |
| 1 | – | 1.06; 1.08; 1.21; 1.43; 1.49; 1.56; 1.59 | – |
| 2 | – | [0.76; 0.78; 0.80; 1.16; 1.16; 1.24; 1.34] | [1.92; 1.94] |
| 3 | – | 1.09; 1.09; 1.21; 1.51; 1.57 | – |
| | – | [0.76; 0.93; 0.93; 1.25; 1.45] | – |
| 4 | – | [0.78; 0.82; 0.88; 1.28; 1.45] | [1.92; 1.94; 1.97] |
| 5 | 3.87 dd (9; 4) | 1.07; 1.11; 1.19; 1.27; 1.33; 1.51; 1.55 | – |
| 7 | 4.06 t (7) | 0.70; 0.82; 0.82; 1.31; 1.34; 1.48; 1.48 | 1.88; 1.90; 1.92; 1.97 |

**Note:** The spectra were taken in deuteropyridine or deuterochloroform. The indices given in square brackets were obtained in deuterochloroform. The spectra of compounds (**2**), (**4**), and (**7**), and also that of compound (**3**) obtained in deuterochloroform, were taken on a Tesla BS 567 A instrument with the internal standard HMDS. The signals of the methyl groups were singlets. Abbreviations: d) doublet; t) triplet; dd) doublet of doublets; q) 1:3:3:1 quartet; td) triplet of doublets.

TABLE 2. Chemical Shifts of the Carbon Atoms of Compounds (**1**), (**3**), (**5**), (**9**), and (**10**) ($\delta$, ppm, $C_5D_5N$, 0 — TMS)

| C atom | Compound | | | | |
|---|---|---|---|---|---|
| | **1** | **3** | **5** | **9** | **10** |
| 1 | 32.13 | 32.24 | 32.20 | 32.17 | 31.83[a] |
| 2 | 31.13 | 31.17 | 31.14 | 30.13[a] | 19.92 |
| 3 | 77.68 | 77.80 | 77.74 | 87.86 | 88.13 |
| 4 | 40.82 | 40.84 | 40.82 | 42.32 | 41.03 |
| 5 | 46.31 | 46.41 | 46.36 | 52.04 | 46.40 |
| 6 | 32.01 | 32.19 | 32.12 | 78.94 | 31.83[a] |
| 7 | 70.07 | 70.39 | 70.42 | 34.26 | 69.95 |
| 8 | 54.78 | 55.25 | 55.34 | 48.37 | 54.63 |
| 9 | 19.48 | 19.79 | 19.96 | 20.61 | 19.52 |
| 10 | 27.66 | 27.44 | 27.36 | 28.71 | 27.35 |
| 11 | 26.91 | 26.58 | 26.75* | 25.89 | 26.85 |
| 12 | 33.12 | 33.22 | 33.40 | 33.12 | 33.10 |
| 13 | 45.75[a] | 46.32 | 45.55 | 45.65 | 45.11 |
| 14 | 45.75[a] | 46.53 | 46.35 | 45.79 | 45.59 |
| 15 | 45.16 | 50.91 | 48.86 | 46.43 | 45.74 |
| 16 | 74.38 | 72.40 | 73.86 | 72.90 | 74.33 |
| 17 | 61.33 | 57.59 | 57.95 | 57.77 | 61.29 |
| 18 | 22.23 | 21.55 | 21.41 | 21.45 | 22.14 |
| 19 | 30.14 | 29.54 | 29.33 | 29.76 | 29.93 |
| 20 | 84.87 | 90.43 | 87.30 | 90.23 | 84.86 |
| 21 | 30.56 | 30.26 | 28.69 | 30.13[a] | 30.57 |
| 22 | 31.84 | 29.90 | 35.02 | 29.86 | 31.67 |
| 23 | 33.58 | 32.94 | 26.48* | 32.77 | 33.54 |
| 24 | 110.60 | 177.50 | 81.67 | 177.24 | 110.58 |
| 25 | 72.83 | – | 71.31 | – | 72.80 |
| 26 | 25.59* | – | 27.11** | – | 25.59* |
| 27 | 25.25* | – | 28.24** | – | 25.23* |
| 28 | 19.64 | 19.73 | 19.90 | 19.94 | 19.60 |
| 29 | 26.18 | 26.20 | 26.21 | 28.40 | 25.70 |
| 30 | 14.75 | 14.75 | 16.79 | 17.05 | 15.32 |
| | | | | *β-D*-Xyl*p* residue | |
| 1 | | | | 107.51 | 107.56 |
| 2 | | | | 75.49 | 75.52 |
| 3 | | | | 78.55 | 78.59 |
| 4 | | | | 71.23 | 71.20 |
| 5 | | | | 67.07 | 67.12 |
| | | | | *α-L*-Rha*p* residue | |
| 1 | | | | 103.90 | |
| 2 | | | | 72.64 | |
| 3 | | | | 71.98 | |
| 4 | | | | 73.78 | |
| 5 | | | | 70.18 | |
| 6 | | | | 18.28 | |

**Note**: Signals marked with the same letter are superposed on one another, and those marked with asterisks are interchangeable.

Thus, the question remained of the stereochemistry of the asymmetric center in the side-chain, and this was answered in the following way. A consideration of Dreiding molecular models showed that the heterocycles in the side chain could be coupled only if the chiral atoms had the 20R,24R or the 20S,24S configurations. Consequently, the elucidation of the configuration of one of the asymmetric atoms would predetermine the stereochemistry of the other center of chirality, as well.

To determine the stereochemistry at C-20, cycloalpigenin was subjected to acid hydrolysis followed by periodate oxidation, which gave the lactone (**3**). The IR spectrum of the latter showed an intense absorption band at 1744 $cm^{-1}$, which is characteristic of a $\gamma$-lactone. In the mass spectrum of lactone (**3**) the maximum peak had *m/z* 99, corresponding to the side-chain. As was to be expected, in the $^1H$ NMR spectrum of compound (**3**), signals were observed from five methyl groups, and the H-16 signal had undergone a downfield shift as compared with that of cycloalpigenin and appeared at 4.94 ppm. In the $^{13}C$ NMR spectrum of the nor- compound (**3**), the C-20 atom resonated at 90.43 ppm. The corresponding atom in the $^{13}C$ NMR spectrum of lactone (**9**), synthesized from cyclocarposide (**8**) [8] for comparison, was observed at 90.23 ppm. The structure of lactone (**9**) was confirmed by its IR and its $^1H$ and $^{13}C$ NMR spectra (see the Experimental section and Table 2). The good agreement of the chemical shifts of the atoms being compared showed identity of the C-20 stereochemistries in compounds (**3**) and (**9**). The above experimental results determined compound (**3**) as (20R)-25-norcycloartane-3$\beta$,7$\beta$,16$\beta$-triol-20,24-olide. Consequently, cycloalpigenin also has the (20R,24R)- stereochemistry of the side-chain.

For confirmation, we made a chemical correlation of the structures of cycloalpigenin (**1**) and cycloalpigenin D (**5**) by passing from the latter to lactone (**3**). Cycloalpigenin D was acetylated with acetic anhydride in pyridine, giving the tetraacetate (**7**) and the previously described triacetate (**6**) [1]. Oxidation of the latter by the Jones reagent [9] at room temperature led to the nor- compound (**4**). The IR spectrum of this compound (**4**) showed, in addition to the absorption bands of ester groups (1735, 1247 $cm^{-1}$), the band at 1773 $cm^{-1}$ that characterizes a $\gamma$-lactone. The $^1H$ NMR spectrum of the product under discussion (**4**) lacked the signals of two methyl groups ($CH_3$-26 and $CH_3$-27) and of H-24. In the mass spectrum of this compound, the maximum peak had *m/z* 99. These facts determined compound (**4**) as (20R)-25-norcycloartane-3$\beta$,7$\beta$,16$\beta$-triol-20,24-olide 3,7,16-triacetate. From the products of its alkaline hydrolysis, after treatment with KU-2 cation-exchange resin and column chromatography, we isolated a compound coinciding in physicochemical constants and spectral indices with lactone (**3**). The formation of lactone (**3**) from cycloalpigenin D confirmed the conclusion of the R-configuration of the C-20 chiral center in the side-chain and also the positions and $\beta$-orientations of all the oxygen functions in the polycyclic part of the cycloalpigenin molecule.

Thus, we are justified in concluding that cycloalpigenin has the structure (20R,24R)-16$\beta$,24:20,24-diepoxy-cycloartane-3$\beta$,7$\beta$,25-triol.

A consideration of the $^1H$ and $^{13}C$ NMR spectra of glycoside (**10**) permitted this glycoside, as well, to be assigned to the cycloartane triterpenoids. *D*-Xylose was found among the products of the acid hydrolysis of cycloalpioside. It was shown by GLC [10] that cycloalpioside is a monoxide. This conclusion was confirmed by the $^1H$ and $^{13}C$ NMR spectra of glycoside (**10**), in which the signals of the $^1H$ and $^{13}C$ nuclei of only one *D*-xylose residue were clearly traced. A comparative analysis of the $^1H$ and $^{13}C$ NMR spectra of cycloalpioside and cycloalpigenin showed that the latter was the genin of the glycoside in question. In the cycloalpioside molecule, the C-3 atom had experienced a glycosylation effect ($\Delta\delta$ +10.45 ppm). The chemical shifts of the carbon atoms and protons of the monosaccharide residue and the SSCCs of the latter showed the pyranose form, the $^4C_1$ conformation, and the $\beta$-configuration of the *D*-xylose.

Thus, cycloalpioside is (20R,24R)-16$\beta$,24:20,24-diepoxycycloartane-3$\beta$,7$\beta$,25-triol 3-O-$\beta$-*D*-xylopyranoside.

## EXPERIMENTAL

For **general observations**, see [11]. The following solvent systems were used: 1) benzene–ethyl acetate (3:1); 2) chloroform–methanol (20:1), 3) chloroform–methanol–water (70:12:1), 4) chloroform–methanol (10:1); and 5) benzene–ethyl acetate (2:1).

$^1H$ and $^{13}C$ NMR spectra were taken on a Bruker AM 400 instrument in deuteropyridine ($\delta$, ppm, 0 — TMS). $^{13}C$ NMR spectra were also recorded under J-modulation conditions.

IR spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer.

**The 3,7-Diacetate of Cycloalpigenin (2) and the 3,16-Diacetate of Cycloalpigenin C from a Mixture of Cycloalpigenin and Cycloalpigenin C.** The intermediate fraction (75 mg) obtained in the isolation of cycloalpigenin C (substance **3**) [1] was acetylated with 0.3 ml of acetic anhydride in 0.7 ml of pyridine at room temperature for 3 days. After evaporation of the solvents, the reaction products were chromatographed on a column, with elution by system 1. This led to the isolation of 17 mg of the diacetate (**2**), $C_{34}H_{52}O_7$, mp 182-183°C (from system 1), $[\alpha]_D^{26}$ +9.1 ± 2° (c 1.1, MeOH). IR spectrum (KBr, $\nu$, $cm^{-1}$) 3300 (OH); 3040 ($CH_2$ of a cyclopropane ring); 1733, 1242 (ester groups). Mass spectrum, *m/z* (%): $M^+$ 572 (1.6), 554 (4.9), 539 (1.4), 512 (100), 497 (11.3), 494 (7.9), 468 (16.2), 452 (90.3), 437 (12.5), 426 (6.9), 419 (6.25), 408 (9.7), 394 (12.5), 339 (19.4), 316 (26.4), 294 (26.4), 279 (30.6), 256 (61.1), 253 (20.8), 243 (18.1), 227 (20.8), 201 (18.1), 199 (20.8), 196 (16.7), 187 (22.2), 185 (30.6), 183 (19.4), 173 (23.6), 171 (22.2), 159 (23.6), 157 (25.0), 143 (52.8). For the $^1H$ NMR spectrum, see Table 1.

On continuing elution of the column with the same system, 55 mg of cycloalpigenin C 3,16-diacetate was isolated [4].

**Cycloalpigenin (1) from (2).** The diacetate (**2**) was hydrolyzed with 3 ml of a 1% methanolic solution of sodium hydroxide at room temperature for 1 h. The appropriate working up and column chromatography in system 2 led to the isolation of 12 mg of cycloalpigenin, $C_{30}H_{48}O_5$, mp 224-226°C (from MeOH), $[\alpha]_D^{24}$ 0 ± 3° (*c* 0.5; MeOH). IR spectrum (KBr, $\nu$, $cm^{-1}$): 3571-3328 (OH), 3038 ($CH_2$ of a cyclopropane ring). Mass spectrum, *m/z* (%): $M^+$ 488 (6.73), 470 (24.04), 455 (7.7), 452 (8.7), 430 (7.7), 429 (7.7), 426 (8.7), 412 (13.5), 395 (6.7), 384 (11.5), 369 (12.5), 331 (9.6), 313 (9.1), 297 (8.7), 274 (17.3), 272 (12.5), 261 (11.5), 259 (12.0), 256 (16.8), 245 (15.4), 243 (15.4), 227 (12.5), 213 (12.5),

209 (11.5), 201 (12.5), 199 (13.5), 196 (38.5), 191 (12.5), 189 (12.5), 183 (11.5), 172 (23.9), 161 (21.7), 159 (23.9), 143 (100), 107 (56.5). For the $^1H$ and $^{13}C$ NMR spectra, see Tables 1 and 2.

**Cycloalpioside (10).** Repeated rechromatography in system 3 of the intermediate fraction accumulated during the separation of substances (**6**) and (**7**) [1] yielded 65 mg of cycloalpioside (**10**), $C_{35}H_{56}O_9$, 277-278°C (from MeOH), $[\alpha]_D^{26}$ — 25.1 ± 2° (*c* 0.71; $C_5H_5N$). IR spectrum (KBr, $\nu$, $cm^{-1}$): 3500-3300 (OH), 3040. ($CH_2$ of a cyclopropane ring.)

GLC [10] showed the presence of one *D*-xylose molecule in cycloalpioside (**10**).

PMR spectrum ($C_5D_5N$, 0 — TMS): 0.27 and 0.78 (2H-19, d, $^2J$ = 4 Hz), 1.04; 1.05; 1.30; 1.42; 1.49; 1.53; 1.56 (7 × $CH_3$, s), 2.64 (H-17, d, $^3J$ = 8 Hz), 3.47 (H-3, dd, $^3J_1$ = 11, $^3J_2$ = 4 Hz), 3.70 (H-5a *D*-xylose, t, $^3J = {}^2J$ = 10 Hz, the H-7 signal is masked by this triplet), 3.99 (H-2 *D*-xytose, t, $^3J$ = 8 Hz), 4.09 (H-3 *D*-xylose, t, $^3J$ = 8 Hz), 4.16 (H-4 *D*-xylose, m), 4.32 (H-5e *D*-xylose, dd, $^2J$ = 10, $^3J$ = 5 Hz), 4.52 (H-16, q, $^3J_1 = {}^3J_2 = {}^3J_3$ = 8 Hz), 4.81 (H-1 *D*-xylose, d, $^3J$ = 8 Hz). For the $^{13}C$ NMR spectrum, see Table 2.

**(20R)-25-Norcycloartane-3β,7β,16β-triol-20,24-olide (3) from (1).** Cycloalpigenin (19 mg) was subjected to acid hydrolysis with 5 ml of a 1% methanolic solution of sulfuric acid at 40°C for 8 h. Then the reaction mixture was diluted with water and treated with chloroform. The chloroform extract was washed with water and evaporated. A solution of the residue in 5 ml of methanol was treated with a solution of 50 mg of sodium periodate in 2 ml of water, and the resulting mixture was left at room temperature for 1 h. The excess of oxidant was destroyed by the addition of one drop of ethylene glycol. The reaction products were poured into water and extracted with chloroform. The chloroform extract was washed with water and evaporated. The residue was chromatographed on a column with elution by system 4. This gave 12 mg of compound (**3**), $C_{27}H_{42}O_5$, mp. 159-160°C; 250-253° (from MeOH), $[\alpha]_D^{24}$ + 92 ± 2° (*c* 0.63; MeOH). IR spectrum (KBr, $\nu$, $cm^{-1}$): 3420 (OH), 3040 ($CH_2$ of a cyclopropane ring), 1744 (γ-lactone). Mass spectrum, *m/z* (%): $M^+$ 446 (9.4), 428 (25), 413 (18.8), 410 (21.9), 395 (15.6), 382 (87.5), 367 (37.5), 349 (28.1), 202 (46.9), 147 (62.5), 145 (65.6), 99 (100). For the $^1H$ and $^{13}C$ NMR spectra, see Tables 1 and 2.

**The 3,7,16,25-Tetracetate (7) and the 3,7,16-Triacetate (6) of Cycloalpigenin D from (5).** Cycloalpigenin D (95 mg) was acetylated with 2 ml of acetic anhydride in 4 ml of pyridine at room temperature for 15 days. The residue after evaporation of the solvents was chromatographed on a column in system 5. This led to the isolation of 10 mg of the amorphous tetraacetate (**7**), $C_{38}H_{58}O_9$, $[\alpha]_D^{24}$ + 133 ± 2° (*c* 0.15; MeOH). IR spectrum, (KBr, $\nu$, $cm^{-1}$): 1736; 1248 (ester groups). Mass spectrum, *m/z* (%): $(M-15)^+$ 643 (0.7), 598 (42), 583 (0.8), 557 (7), 554 (3), 538 (39), 523 (6), 496 (4.5), 494 (3), 478 (22), 463 (9), 437 (9), 418 (10), 403 (9), 377 (6), 279 (6), 253 (9), 185 (50), 149 (55), 125 (100). For the $^1H$ NMR spectrum, see Table 1.

Continuing elution of the column with the same system yielded 81 mg of the triacetate (**6**), described previously [1].

**(20R)-25-Norcycloartane-3β,7β,16β-triol-20,24-olide 3,7,16-Triacetate (4) from (6).** The triacetate (**6**) (81 mg) in 4 ml of acetone was oxidized with 0.1 ml of the Jones reagent [9] at room temperature for 15 min. The excess of oxidant was destroyed by the addition of 1 ml of methanol. After the usual working up, column chromatography in system 5 yielded 68 mg of compound (**4**), $C_{33}H_{48}O_8$, mp. 217-220°C (from MeOH), $[\alpha]_D^{24}$ + 113 ± 2° (*c* 0.88; MeOH). IR spectrum (KBr, $\nu$, $cm^{-1}$): 1773 (γ-lactone), 1735; 1247 (ester groups). Mass spectrum, *m/z* (%): $(M-60)^+$ 512 (20), 452 (45), 437 (16), 377 (26), 99 (100). For the $^1H$ NMR spectrum, see Table 1.

**(20R)-25-Norcycloartane-3β,7β,16β-triol-20,24-olide (3) from (4).** Compound (**4**) (56 mg ) was hydrolyzed with 3 ml of a 1% methanolic solution of sodium hydroxide at room temperature for 15 days. The reaction mixture was diluted with methanol and neutralized with KU-2 cation-exchange resin. The residue after removal of the resin and evaporation of the solvent was chromatographed on a column, with elution by system 4. This gave 30 mg of a product identified as lactone (**3**) from its physicochemical constants, a direct TLC comparison, and the indices of its IR, $^1H$ NMR, and mass spectra.

**(20R)-25-Norcycloartane-3β,6∝,16β-triol-20,24-olide 6-O-α-*L*-Rhamnopyranoside 3-O-β-*D*-Xylopyranoside (9) from (8).** In three stages, cyclocarpioside (**8**) [8] was converted by the method of [12] into the lactone (**9**), $C_{38}H_{60}O_{13}$, mp. 230-235°C (from MeOH), $[\alpha]_D^{24}$ 0 ± 3° (*c* 0.925; MeOH). IR spectrum (KBr, $\nu$, $cm^{-1}$): 3510-3370 (OH), 1760 (γ-lactone). PMR spectrum ($C_5D_5N$, 0−TMS): 0.23 and .044 (2H-19, d, $^2J$ = 4 Hz), 0.93; 1.12; 1.38; 1.49; 1.54 (5 × $CH_3$, s), 1.56 ($CH_3$ *L*-rhamnose, d, $^3J$ = 5 Hz), 2.58 (H-17, d, $^3J$ = 8 Hz), 4.78 (H-1 *D*-xylose, d, $^3J$ = 8 Hz), 4.87 (H-16, m), 5.32 (H-1 *L*-rhamnose, s). For the $^{13}C$ NMR spectrum, see Table 2.

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