with 0.2 M sodium dihydrogen phosphate in the butanol-acetone-water (4:5:1) system and by
GLC-mass spectrometry in the form of the corresponding aldonitrile peracetates. L-arabinose
and 2,4-di-O-methyl-D-xylose were identified.

High-Temperature Hydrogenation of Culcitosides C₂ and C₃. Hydrogenation was performed
with a mixture of 3 mg of a glycoside and 300 mg of catalyst [5% Pd/CaCO₃] as described in
[8]. 24-Methylcholesterol was hydrogenated similarly. 24-Methylcholestanate was identified
in the reaction products by GLC and GLC-MS.

SUMMARY

Two new steroid glycosides have been isolated from the starfish Culcita novaeguineae
and characterized: 246-methyl-5α-cholestan-3β,4β,6α,8,15β,16β,28-heptanol 28-O-[O-(2,4-
di-O-methyl-β-D-xylopyranosyl)-(1→2)-α-L-arabinopyranoside] – culcitoside C₂ – and its
4-deoxy analogue – culcitoside C₃.

LITERATURE CITED

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WITHASTEROIDS OF Physalis.

VII. 14α-HYDROXYIXOCARLANOLIDE AND 24,25-EPOXYWITHANOLIDE D

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and N. K. Abubakirov

Two new withasteroid have been isolated from Physalis angulata L. – 14α-hydroxy-
ixocarpanolide and 24,25-epoxywithanolide D. 14α-hydroxyixocarpanolide –
C₂₈H₄₀O₇, mp 245-250°C (from methanol), [α]D²₀+29 ± 2° (chloroform). 24,25-
Epoxywithanolide D – C₂₄H₃₈O₇, mp 257-261°C (from methanol, [α]D²₆ +23 ± 2°
(chloroform). On the basis of its UV, IR, CD, mass, and ¹H and ¹³C NMR spectra
the structure of 5α,14α,20R-trihydroxy-1-oxo-6α,7α-epoxy-22R-witha-2-enolide is
suggested for 14α-hydroxyixocarpanolide. On the basis of spectral characteristics
and the preparation of 48-acetoxy and 4-oxo derivatives of 24,25-epoxywithanolide
D, the structure of 48,20R-dihydroxy-1-oxo-5β,6β;24S,25S-diepoxy-22R-witha-2-
enolide is proposed for it.

We have begun an investigation of the plant Physalis angulata L. (Solanaceae) growing
in the territory of Tashkent province. As a result of the chromatographic separation of an
extract we have obtained several compounds belonging, according to their spectral character-
istics, to the withasteroids.

Institute of the Chemistry of Plant Substances of the Uzbek SSR Academy of Sciences,
Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 596-602, September-
The UV spectrum of withasteroid (I) has an absorption maximum at 225 nm (ε 10,370) and in the IR spectrum a band at 1683 cm⁻¹ showing the presence of an α,β-unsaturated carbonyl group. The PMR spectrum (Table 1) has a doublet at 6.02 ppm and a doublet of triplets at 6.57 ppm, which are characteristic for the H-2 and H-3 protons, respectively, at a conjugated double bond in ring A. An analysis of the multiplicities of the signals showed that the H-2 atom interacts vicinally with H-3 (J = 10.0 Hz) and allylically with one of the protons at C-4 (J = 2.7 Hz). The proton at C-3 experiences vicinal spin-spin coupling with H-2 (J = 10.1 Hz) and with the methylene protons at C-4 (mJ = 5.1 and 2.1 Hz). These characteristics of the PMR spectrum, and also the presence in the ¹³C NMR spectrum (Table 2) of signals at 203.5 ppm (C-1), 129.2 ppm (C-2), and 140.3 ppm (C-3) unambiguously show the presence of a 1-keto-2,3-ene grouping in ring A [1].

A doublet at 3.09 ppm with J = 4.0 Hz and a doublet of doublets at 3.49 ppm with J = 4.0 and 1.7 Hz in the PMR spectrum of withasteroid (I), which are assigned to H-6 and H-7, fall into the region characteristic for protons geminal to an epoxide group. The doublet nature of the signal at 3.09 ppm means that H-6 interacts only with one proton (H-7); there is no proton at C-5. The values of the spin-spin coupling constants, SSCCs, and of the chemical shifts of the H-6 and H-7 signals indicate the α orientation of the epoxy group [2]. The substituent at C-5 is also α-oriented, as is shown by the negative absorption band at 338 nm in the CD spectrum [3].

Although the IR spectrum of the withasteroid (I) has a band at 3575 cm⁻¹ corresponding to the vibrations of the OH groups, compound (I) cannot be acetylated, and in the PMR spectrum there are no signals of protons geminal to hydroxy groups. Consequently, all the hydroxy groups present are tertiary. One of the hydroxy groups is located at C-5, as is shown unambiguously by a singlet at 73.7 ppm in the ¹³C spectrum. This is confirmed by the chemical shifts of doublets at 55.7 and 54.5 ppm (Table 2), belonging to C-6 and C-7, respectively [4]. Thus, the substitution of rings A and B of the steroid moiety of compound (I) and that of isocarpanolide (V), isolated from Physalis ixocarpa Brot. [2], are identical.

An absorption band of withasteroid (I) in the IR spectrum at 1735 cm⁻¹, two doublet signals in the PMR spectrum (0.88 and 1.17 ppm), the position of the signals from C-22 and C-26 in the ¹³C NMR spectrum (Tables 1 and 2) [1, 2] and an ion with m/z 127 in the mass spectrum show that the lactone present in the side chain is six-membered and is saturated. The CD spectrum shows a negative Cotton effect at 218 nm (Δε = -0.98) due to the n-π* transition of a saturated lactone [5]. A positive effect at 240 nm (Δε = +0.27) shows the R configuration at C-22. All this enabled us to come to the conclusion that the lactones of

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TABLE 1. Chemical Shifts* and Spin-Spin Coupling Constants (δ, ppm; J, Hz; C₆D₆N; 0 - TMS) of the Protons of 14α-Hydroxycarpanolide (I), 24,25-Epoxywithanolide D (II), and 24,25-Epoxywithanolide D Acetate (III).

<table>
<thead>
<tr>
<th>Proton</th>
<th>Compound</th>
<th>I</th>
<th>II</th>
<th>III**</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-2</td>
<td>6.02 dd</td>
<td>6.47 d</td>
<td>6.50 d</td>
<td></td>
</tr>
<tr>
<td>H-3</td>
<td>6.57 ddd</td>
<td>7.26 dd</td>
<td>7.2 dd</td>
<td></td>
</tr>
<tr>
<td>H-4</td>
<td>6.50 d</td>
<td>4.03 d</td>
<td>5.05 d</td>
<td></td>
</tr>
<tr>
<td>H-4</td>
<td>7.21 dt</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>H-6</td>
<td>3.09 d</td>
<td>3.25 br.s</td>
<td>3.37 br.s</td>
<td></td>
</tr>
<tr>
<td>H-7</td>
<td>2.57 dd</td>
<td>2.71 dt</td>
<td>2.12 m</td>
<td></td>
</tr>
<tr>
<td>H-22</td>
<td>4.43 dd</td>
<td>4.67 dd</td>
<td>4.66 m</td>
<td></td>
</tr>
<tr>
<td>H-25</td>
<td>5.12 m</td>
<td>0.96 s</td>
<td>0.94 s</td>
<td></td>
</tr>
<tr>
<td>CH₃-18</td>
<td>1.42 s</td>
<td>1.42 s</td>
<td>1.45 s</td>
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</tr>
<tr>
<td>CH₂-19</td>
<td>1.27 s</td>
<td>1.84 s</td>
<td>1.70 s</td>
<td></td>
</tr>
<tr>
<td>CH₂-24</td>
<td>1.42 s</td>
<td>1.47 s</td>
<td>1.66 s</td>
<td></td>
</tr>
<tr>
<td>CH₂-27</td>
<td>1.17 d</td>
<td>1.64 s</td>
<td>1.33 s</td>
<td></td>
</tr>
<tr>
<td>CH₂-28</td>
<td>0.88 d d</td>
<td>1.34 s</td>
<td>1.92 s</td>
<td></td>
</tr>
</tbody>
</table>

*dd - doublet; dd - doublet of doublets; dt - doublet of triplets; ddd - doublet of quartets; m - multiplet; s - singlet; br.s - broadened singlet.

**Spectrum taken with the addition of trifluoroacetic acid.