WITHASTEROIDS OF Physalis.

VIII. VAMONOLIDE

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A new withasteroid — vamonolide — has been isolated from the epigeal part of *Physalis angulata* L. (Solanaceae). On the basis of spectral characteristics, its structure has been established as 5α,14α-dihydroxy-1-oxo-6α,7α-epoxy-20R, 22R-with-2-enolide.

Continuing a study of the epigeal part of *Physalis angulata* L. (Solanaceae) [1], we isolated a new compound, vamonolide (I), which was assigned on the basis of its total spectral characteristics to the withasteroid group. Its UV spectrum had a maximum at 223 nm and its IR spectrum an absorption band at 1690 cm^{-1} characteristic for a conjugated carbonyl group. In the PMR spectrum (Table 1), the signals of two vinyl protons undergoing, respectively, allyl and vicinal interactions with two methylene protons appeared clearly at 6.03 and 6.57 ppm. All this indicated the presence of an α,β-unsaturated carbonyl group in ring A [2]. In addition to those already mentioned, the PMR spectrum of vamonolide (I) contained signals at 3.10 and 3.49 ppm of protons geminal to an epoxide group [3]. Similar signals have been reported previously in the spectra of 14α-hydroxyixocarpanolide (II) [1] and ixocarpanolide (III) [4] and have been assigned to H-6 and H-7. When H-7 (3.49 ppm) was irradiated with a radiofrequency field, the doublet of the H-6 proton (3.10 ppm) was converted into a singlet. This showed the absence of a proton at C-5. The spin-spin coupling contants (SSCCs) of the H-6 and H-7 protons ($J_{6,7}$ = 4.0 and $J_{7,8}$ = 2.0 Hz) showed the α-orientation of the epoxide function.

In the mass spectrum of compound (I), the peak of an ion with m/z 125 was observed which, as is well known, appears when either an α,β-unsaturated lactone group is present in the side chain [5], or a 5α-dihydroxy-1-oxo-2-ene group is present in ring A [6]. Since the available spectral characteristics [absorption band at 1748 cm^{-1} in the IR spectrum, the signals of two methyl groups in the form of a doublet in the PMR spectrum, and also the elementary composition of the $C_9H_{16}O_2$ ion (m/z 156.1258), corresponding to the side chain (C-17—C20 cleavage)] were evidence in favor of a six-membered cyclic lactone, the ion with m/z 125 could be formed only from ring A. Consequently, one of the hydroxy groups of the withasteroid (I) was present at C-5. Its α-orientation was determined with the aid of circular dichroism, which showed a negative Cotton effect at 339 nm [7].

The Cotton effects in withasteroids (I-III) in the 215-340 nm region are as follows:

Compound			
I	$\Delta\varepsilon_{339}$ −2.22	$\Delta\varepsilon_{240}$ +0.55	$\Delta\varepsilon_{215}$ −1.93
II	$\Delta\varepsilon_{338}$ −1.37	$\Delta\varepsilon_{240}$ +0.27	$\Delta\varepsilon_{218}$ −0.98
III	$\Delta\varepsilon_{339}$ −2,39	$\Delta\varepsilon_{242}$ +0,29	$\Delta\varepsilon_{221}$ −1.56

As shown above, in all the compounds being compared the substitution in rings A and B was the same. The spectral characteristics do not contradict, either, the assumption that the substitution of rings C and D of vamonolide coincides with the pattern of substitution of 14α-hydroxyixocarpanolide (II). Moreover, the identity of the structures of the side-chain lactone group followed from the peaks of an ion with m/z 127 observed in the mass spectra of the compounds, from the two doublet signals of methyl groups in the PMR spectra, and from the coincidence in the CD spectra of the sign and order of magnitude of the Cotton effect. Thus, compounds (I-III) each had a saturated six-membered lactone ring with methyl groups having the 24α,25β position and orientation [1, 4, 8].

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TABLE 1. Chemical Shifts* and Spin-Spin Coupling Constants (δ, ppm; J, Hz; C_5D_5N, 0 – TMS) of the Protons of Vamonolide (I), of 14α-Hydroxyixocarpanolide (II), and of Ixocarpanolide (III)

Proton	Compound		
	I	II [1]	III [4]
H-2	6,03 dd $^3J=10,1$; $^4J=2,8$	6,02 dd $^3J=10,1$; $^4J=2,7$	6,03 dd $^3J=10,0$; $^4J=2,8$
H-3	6,57 dddd $^3J=10,1$; 5,1 and 2.3	6,57 dddd $^3J=10,1$; 5,1 and 2,1	6,57 dddd $^3J=10,0$; 5,0 and 2,0
H-4	2,57 dd $^2J=18,8$; $^3J=5,1$	2,57 dd $^2J=18,8$; $^3J=5,1$	2,56 dd $^2J=18,8$; $^3J=5,0$
H-4	2,72 dt $^2J=18,8$; $^3J=2,3$; $^4J=2,8$	2,71 dt $^2J=18,8$; $^3J=2,1$ $^4J=2,7$	2,69 dt $^2J=18,8$; $^3J=2,0$ $^4J=2,8$
H-6	3,10 d $^3J=4,0$	3,09 d $^3J=4,0$	3,12 d $^3J=3,8$
H-7	3,49 dd $^3J=4,0$ dt and 2.0	3,49 dd $^3J=4,0$ and 1,7	3,26 m $^3J=3,8$ and 2,2
H-22	4,40 dt $^3J=11,8$; 3,1 and 2.9	4,43 dd $^3J=11,7$ and 2.9	4,39 dd $^3J=11,5$ and 2.9
H-25	2,17 m $^3J=8,5$ and 6.7	2,12 m $^3J=9,3$ and 6.6	2,18 $^3J=9,4$ and 6.7
CH_3-18	0,86 s	1,42 s	1,18 s
CH_3-19	1,28 s	1,27 s	1,21 s
CH_3-21	0,87 d J=6 3	1,42 s	1,39 s
CH_3-27	1,22 d $^3J=6,7$	1,17 d $^3J=6,6$	1,22 d $^3J=6,7$
CH_3-28	0,93 d $^3J=6,6$	0,88 d $^3J=6,6$	1,06 d $^3J=6,6$

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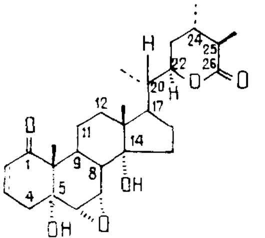
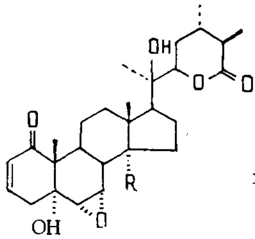
*s – singlet; d – doublet; dd – doublet of doublets; dt – doublet of triplets; m – multiplet.



I



II. R = OH

III. R = H

The same peaks of an ion with m/z 299 were observed in the mass spectra of compounds (I) and (II) (28.5 and 31.5%, respectively). This ion is formed as the result of C-17–C-20 cleavage and the loss of a water molecule [9]. The peaks of ions belonging to the side chains of compounds (I) and (II) (m/z 156 and 172, respectively), differed by 16 mass units. Consequently, there was no hydroxy group in the side chain of vamonolide (I).

Three doublet signals of methyl groups were observed in the PMR spectrum of compound (I). Two of them (at 1.22 and 0.93 ppm) were assigned to the CH_3-27 and CH_3-28 groups of the saturated lactone ring and the third must be assigned to CH_3-21, which confirmed the absence of a substituent at C-20.

Thus, vamonolide (I) is 5α,14α-dihydroxy-1-oxo-6α,7α-epoxy-20R,22R-witha-2-enolide [10].

EXPERIMENTAL

General observations and the instruments used are given in [1, 4].

Isolation of Vamonolide (I). As shown previously [1], the chromatography of an extract of *Physalis angulata* L. on a column in the chloroform–acetone (5:1) system yielded several fractions. The subsequent rechromatography of fractions 6-8 and, additionally, fraction 9 (total weight 0.130 g) in the chloroform–methanol (20:1) and chloroform–acetone (8:1) systems led to vamonolide (0.104 g). The yield amounted to 0.0015% of the weight of the air-dry raw material.

Vamonolide (I), $C_{28}H_{40}O_6$, mp 243-247°C (from methanol), $[\alpha]_D^{23}$ 24.9 ± 2° (c 0.97; methanol); $\lambda_{max}^{C_2H_5OH}$: 223 nm (ε 11750); ν_{max}^{KBr}, cm^{-1}: 3530-3485, 2940, 1748, 1690. Mass spectrum, m/z (%): M^+ 472 (2.4); 454 (2.9), 436 (2.9), 348 (5.9), 316 (11.8), 299 (28.5), 298 (100), 252 (29.4), 185 (14.7), 174 (20.2), 156 (17.8), 145 (16.2), 127 (12.6), 125 (53.0), 121 (25), 97 (50).

SUMMARY

A new withasteroid – vamonolide – has been isolated from the leaves of Physalis angulata L. It has the structure of 5α,14α-dihydroxy-1-oxo-6α,7α-epoxy-20R,22R-witha-2-enolide.

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