SUMMARY

1. The glycosylation of 20(S),24(R)-epoxydammarane-3α,12β,25-triol in the presence of insoluble silver compounds has been studied.

2. 20(S),24(R)-Epoxydammarane-3α,12β,25-triol 3-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) and its 3,12-di-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) have been synthesized for the first time.

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WITHASTEROIDS OF *Physalis*.

V. A STUDY OF THE ^1H AND ^{13}C NMR SPECTRA OF THE WITHASTEROIDS VISCONOLIDE AND 28-HYDROXYWITHAPERUVIN C

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UDC: 547.926+543.422+541.67

The PMR and ^{13}C NMR spectra of new withasteroids — visconolide and 28-hydroxywithaperuvin C, isolated from *Physalis viscosa* L. — have been investigated. A detailed analysis of the spectral characteristics obtained is given. For visconolide is proposed the structure of 4β,12α,17β,20R,28-pentahydroxy-1-oxo-5β,6β-epoxy-22R-witha-2,24-dienolide, and for 28-hydroxywithaperuvin C that of 6β,14α,17β,20R,28-pentahydroxy-1-oxo-22R-witha-2,4,24-trienolide.

Continuing a study of the withasteroids of *Physalis viscosa* L. [1-4], we have isolated three new compounds from this plant.

A withasteroid with the composition $C_{28}H_{38}O_7$, mp 172-173°C, $[\alpha]_D^{22}$ —83±2° was identified on the basis of a comparison of spectral characteristics and physicochemical constants of the compound itself and of its acetyl derivative as withaperuvin C isolated previously from the roots of *Physalis periviana* L. [6]. The other two compounds were present in the plant in minor amounts and are new. A withasteroid with the composition $C_{28}H_{38}O_9$, we have called visconolide (I), and the second compound, with the composition $C_{28}H_{38}O_8$, is 28-hydroxywithaperuvin C (III).

Visconolide (I). An intense maximum in the UV spectrum at 220 nm (log ε 4.14) and an absorption band in the IR spectrum at 1690 cm^{-1} showed that compound (I) contained an α,β-unsaturated lactone ring. The mass spectrum contained the peaks of ions with m/z 185 (24%)

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 657-663, September-October, 1985. Original article submitted December 6, 1984.

 0009-3130/85/2105-0616$09.50

TABLE 1. Chemical Shifts and Spin-Spin Coupling Constants (δ, ppm; J, Hz; C_5D_5N; O — TMS) of the Protons of Visconolide (I), of 28-Hydroxywithaperuvin C (III), and of Their Acetyl Derivatives (II and IV)

Compound	Positions of the protons*										
	H-2	H-3	H-4	H-6	H-22	CH_3-18	CH_3-19	CH_3-21	CH_3-27	CH_2OH	OAc
I	6,45 d	7,19 q	4,03 d	3,36	5,35 q	1,33 s	1,81 s	1,87 s	2,05 br.d	4,43; 4,73	—
	^3J=10,0 Hz	^3J=10.0 and 6.4 Hz	^3J=6 4 Hz	br.s	^3J=13,5 and 3.1 Hz				J≃1,6 Hz	2d, ^2J=14,4Hz	
II	6,49 d	7,15 q	5,04 d	3.49	5,27 q	1.39 s	1,77 s	1,77s	2,07 br.s	4,78; 5,04	1,90;
	^3J=9,9 Hz	^3J=9,9 and 6.3 Hz	^3J=6,3 Hz	br.s	^3J=13,3 and 2.8 Hz					2d, ^2J=13,6Hz	2,07
III	6,20 d	6.91 q	6,15 d	4,94	5,37 q	1,48 s	1,95 s	1,83 s	2,06 br.d	4,44; 4,74	—
	^3J=9,7 Hz	^3J=9,7 and 6,0 Hz	^3J=6,0 Hz	br.t ^3J=6,8 Hz	^3J=13,4 and 3,1 Hz				J≃1,6 Hz	2d, ^2J=14,4Hz	
IV	6,22 d	6,91 q	6,34 d	5,79 br.t	5,27 q	1,53 s	1,63 s	1,76 s	2,05 br.s	4,70; 5,00	2,02;
	^3J=9,7 Hz	^3J=9 7 and 6,0 Hz	^3J=6,0 Hz	^3J=5 Hz	^3J=13.1 and 2.1 Hz					2d, ^2J=13,5Hz	2,05

*d — doublet; q — quartet; br.s — broadened singlet; br.t — broadened triplet; s — singlet.

TABLE 2. Chemical Shifts of the Carbon Atoms in the ^{13}C NMR Spectra of Visconolide (I) and of 28-Hydroxywithaphysanolide (VI) [4] (C_5H_5N; δ, ppm; TMS — 0)*

C atom	Compound		C atom	Compound	
	I	VI		I	VI
1	202.4	203.9	15	30.3	29.9
2	132.4	130 3	16	37.2	37,2
3	144.5	145.9	17	88,2	88.4
4	70,4	69,1	18	19 6	19,8
5	64,4	139.3	19	16 6	21,1
6	60.9	128,5	20	79,4	79,4
7	26 6	26.5	21	20,7	22,5
8	34,7	36,6	22	82 6	82,8
9	37,7	37,3	23	29,9	30,9
10	48.5	50,1	24	154.5	154.4
11	21,6	23.2	25	120.9	121,0
12	32.9	33,1	26	167,1	167,1
13	54 8	54 9	27	11 9	11 9
14	81,9	81.9	28	60.9	60,9

*The assignment of the signals was made on the basis of the results of a comparative study of the ^{13}C NMR spectra taken under the conditions of complete and partial suppression of spin-spin coupling with protons and by an analysis of the values of the chemical shifts of the carbon atoms with the bringing in of the characteristics of the spectra of 28-hydroxywithaphysanolide (VI) [4], 4β-hydroxywithanolide E (VII) [4] and its acetate [11], and also other withasteroids [7, 11, 12].

and 141 (64%), indicating the presence of a hydroxy group attached to the lactone ring and the cleavage of the bond between the C-17 and C-20 atoms bearing a diol grouping.

The PMR spectrum of visconolide (I) recorded in deuterated pyridine with the addition of trace amounts of trifluoroacetic acid was characterized by the presence of the signals of four methyl groups (singlets of 3 H each at 1.33, 1.81, and 1.87 ppm and a doublet with J = 1.6 Hz having broadened components at 2.05 ppm); of a hydroxymethyl group (doublets of 1 H each at 4.43 and 4.73 ppm with ^2J = 14.4 Hz); of the H-22 proton of the lactone ring (quartet at 5.35 ppm with ^3J = 13.5 and 3.1 Hz); or protons located in ring A at a double bond conjugated with a carbonyl group (doublet at 6.45 ppm with ^3J = 10.0 Hz for H-2 and quartet at 7.19 ppm with ^3J = 10.0 and 6.4 Hz for H-3 [9, 10]; of a proton geminal to a secondary hydroxy group (doublet at 4.03 ppm with ^3J = 6.4 Hz for H-4); and of a proton at an epoxy group (broadened singlet with $W_1/_2$ = 4.5 Hz at 3.36 ppm for H-6). It was established by double proton-proton resonance that the doublet nature of the singlet at 4.03 ppm was due to a vicinal interaction of H-4 with H-3, and that H-6 interacted with the protons of the neighboring methylene group at C-7 with a constant ^3J < 2 Hz. These facts show not only the position of the secondary hydroxy group at C-4 and of the epoxy group at C-5 and C-6, but also their β-axial orientation.

The acetylation of visconolide (I) gave the diacetyl derivative (II). The PMR spectrum of this compound showed, in addition to the singlets of two acetyl groups at 1.89 and 2.06 ppm, a paramagnetic shift of the signals of the H-4 atom and of the protons of the hydroxymethyl group.

The parameters of the PMR spectra of visconolide (I) and of the diacetate (II) (Table 1), with the exception of the characteristics of the protons of the lactone moiety of the molecule, were extremely close to those of 4β-hydroxywithanolide E (VII) and its acetyl derivative [3, 8]. The ^{13}C chemical shifts of the carbon atoms of the steroid part of the withasteroid that we are describing (I) (Table 2) and of 4β-hydroxywithanolide E (VII) [4] were identical.

The facts given above permit the statement that the structures of the steroid moieties of the molecules of visconolide (I) and of 4β-hydroxywithanolide E (VII) are identical. This was confirmed by the fact that when withasteroid (I) was oxidized with the Jones reagent a product was obtained that was identified as 14α-hydroxy-5β,6β-epoxyandrost-2-ene-1,4,17-trione (V).

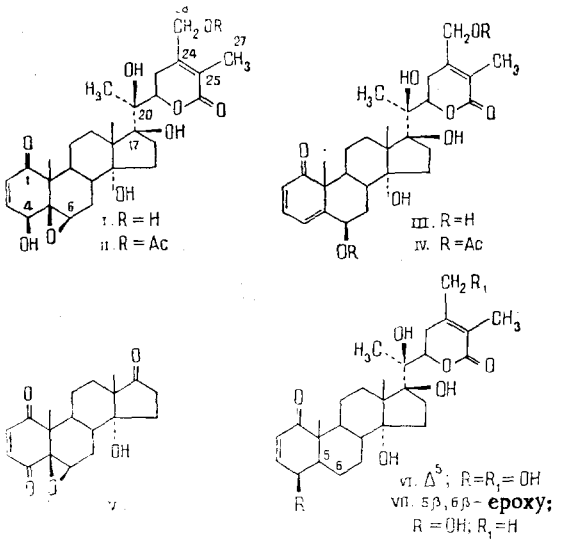
Earlier [4], in analyzing the results of an investigation of the characteristics of the ^{13}C NMR spectra of a number of withasteroids, we showed that the values of the chemical shifts of the C-23, C-24, C-25, C-27, and C-28 carbon atoms change substantially in definite dependence of the position of the hydroxymethyl group in the lactone ring. In the present work these characteristics were used as a criterion for determining whether visconolide (I) belonging to the 27-hydroxy- or the 28-hydroxywithasteroid series.

In the ^{13}C NMR spectrum of visconolide (I) the methyl and hydroxymethyl groups which are conjugated with a double bond, are characterized by signals at 11.9 and 60.9 ppm, while the C-23, C-24, and C-25 carbon atoms of the α,β-unsaturated acetone ring resonate at 29.9, 154.5, and 120.9 ppm, respectively (see Table 2). The above-mentioned chemical shifts are identical with those of the 28-hydroxywithaphysanolide (VI) described previously (see Table 2) and do not correlate at all with those for 27-hydroxywithasteroids (withastramonolide, withaferin A) [4]. This means that the compound (I) under investigation belongs to the 28-hydroxywithasteroid series.

The identical values of the chemical shifts of the carbon atoms from C-1 to C-21 of visconolide (I) and of 4β-hydroxywithanolide E (VII) [4] is an important proof not only of identical structures of the steroid moieties of the two molecules but also of the same configurations of the substituents at the asymmetric centers.

Thus, the combination of experimental facts given above permits visconolide (I) to be determined as 4β,14α,17β,20R,28-pentahydroxy-1-oxo-5β,6β-epoxy-22R-witha-2,24-dienolide.

28-Hydroxywithaperuvin C (III). This withasteroid was the most polar among the compounds that we isolated from *Physalis viscosa* L. In its IR spectrum, in addition to the absorption band at 1690 cm^{-1} of an α,β-unsaturated lactone carbonyl, there was a band at 1660 cm^{-1}, which is characteristic for a conjugated carbonyl group in a six-membered ring. The absorption maximum in the UV spectrum at 317 nm (log ε 3.58) corresponds to that of withaperuvin C [6].



In the PMR spectrum of compound (III) (C_5D_5N) the signals of three olefinic protons were observed: a doublet at 6.20 ppm with ^3J = 9.7 Hz (H-2); a quartet at 6.91 ppm with ^3J = 9.7 and 6.0 H (H-3); and a doublet at 6.15 ppm with ^3J = 6.0 Hz (H-4). The splitting of the lines of the signals mentioned is due to the spin-spin coupling of these protons in the manner of an ABC system. The facts given indicate the presence of a 2,4-dien-1-one grouping in the molecule of the withasteroid (III).

The IR spectrum of compound (III) showed the presence of hydroxy groups. Fragments with m/z 185 and 141 in its mass spectrum and the 100% fragments with m/z 168 and 123 in the spectrum of the acetate (IV) show that one of the hydroxy groups is present in the lactone ring of the side chain.

In the PMR spectrum of (III) there are signals of a triplet nature with Σ^3J = 6.8 Hz at 4.94 ppm (see Table 1) the lines of which are broadened. Under the conditions of double proton-proton resonance, with saturation of the resonance transitions of the H-4 nuclei, this

broadening is eliminated. Consequently, the triplet under consideration at 4.94 ppm belongs to the H-6 proton, since only this can experience allyl coupling with H-4. In the spectrum of the diacetate (IV), the H-6 signal is present in a considerably weaker field; namely, at 5.73 ppm. From this we are justified in concluding that a secondary hydroxy group is present at C-6 and, according to the index Σ^3J = 6.8 Hz for H-6, it has the β-quasi-axial orientation.

In the region of resonance of the protons of methyl groups there are four signals of 3 H each: singlet at 1.48 (CH_3—18), 1.83, and 1.95 ppm (CH_3-19 and CH_3-21) and a doublet with broadened lines at 2.05 ppm with J = 1.6 Hz. The signals of the H-22 proton appears in the form of a quartet with ^3J = 13.4 and 3.1 Hz at 5.37 ppm, which is characteristic of withasteroids containing a diol grouping at C_{17} and C-20.

On the basis of the experimental facts given, and also in consideration of the simultaneous presence of withaperuvin C [6] and the compounds under investigation in the plant, we may conclude that the withasteroid (III) is a hydroxy analog of withaperuvin C with the hydroxy group in the lactone ring.

The presence in the PMR spectrum of compound (III) of the signal of only one methyl group at a double bond (2.05 ppm) and also of the protons of a hydroxymethyl group (doublets at 4.44 and 4.74 ppm with ^2J = 14.4 Hz) led us to the conclusion that the hydroxy group was located in the lactine ring at C-27 and C-28.

The resonance characteristics of the protons of the lactone rings of compound (III), of 28-hydroxywithaphysanolide [4], and of visconolide and their acetates are extremely similar to one another (H-22, CH_2OH, and CH_3-27 in Table 1), in contrast to those of the 27-hydroxywithasteroids [5, 13, 14].

Thus, compound (III) is 28-hydroxywithaperuvin C and has the structure of 6β,14α,17β,20R,28-pentahydroxy-1-oxo-22R-witha-2,4,24-trienolide.

To confirm the correctness of the conclusion made, the diacetate of 28-hydroxywithaperuvin C (IV), the diacetate of 28-hydroxywithaphysanolide [4], and the acetate of withaperuvin C [6] were oxidized at the C17—C-20 diol grouping under the same conditions (by Jones' method). The reaction products were separated into steroid and lactone fractions. On chromatographic comparison, the steroid fragment of the diacetate of 28-hydroxywithaperuvin C (IV) coincided with the analogous fragment of the acetate of withaperuvin C and the lactone moiety of the diacetate of (III) with the corresponding fragment of the side chain of the diacetate of 28-hydroxywithaphysanolide.

It must be mentioned that in contrast to the withasteroids from *Ph. viscosa* of North American origin [7, 12], which contain a β-orientated side chain, all the compounds that we isolated from *Ph. viscosa* L. growing in Central Asia, contained only α-oriented side chains. Six of them form three pairs: withaperuvin C—28-hydroxywithaperuvin C; withaphysanolide [2]—28-hydroxywithaphysanolide [4]; and 4β-hydroxywithanolide E [3]—visconolide, differing by the presence of a methyl or hydroxymethyl group at C-24 of the lactone ring. This is the first time that this position of the hydroxy group has been described. Again, we did not detect in *Ph. viscosa* withasteroids having a 13,14-seco-16,24-cyclo structure with a C-14—C-27 ether bond, which are extremely characteristic for the genus *Physalis*. Apparently, the α orientation of the side chain makes the molecule more stable and inhibits possible intramolecular transformations.

EXPERIMENTAL

General Observations. PMR spectra were recorded on a Varian SC-300 spectrometer in the Fourier regime at 30°C, and ^{13}C NMR spectra on a Varian CFT-20 instrument with TMS as internal standard. Sulifol UV-254 was used for thin-layer chromatography in the following solvent systems: 1) hexane—acetone (1:1); 2) hexane—acetone (2:3); 3) chloroform—benzene—methanol (5:5:1); and 4) benzene—ethyl acetate (1:1). For other general information, see [4].

Isolation of the Withasteroids. By washing the column with hexane—acetone (2:3), in addition to 28-hydroxywithaphysanolide [4], another three withasteroids were obtained which, after rechromatography in the chloroform—ethanol (10:1) system, were crystallized from methanol. The Rf values in system 2 of the withasteroids isolated were: withaperuvin C [6] — 0.59; 28-hydroxywithaphysanolide — 0.39; visconolide (I) — 0.36; 28-hydroxywithaperuvin C (III) — 0.28.

Withapeuvin C – $C_{28}H_{38}O_7$, mp 172-173°C (from methanol); $[\alpha]_D^{20}$ – 83±2° (*c* 2,33; methanol). $\lambda_{max}^{C_2H_5OH}$: 230, 318 nm (log ε 4.05, 3.55); ν_{max}^{KBr}, cm^{-1}: 3350, 1690, 1680, 1660, 1635, 1580; mass spectrum, m/z (%): 468(5), 450(24), 432(4), 343(11), 299(25), 281(51), 238(68), 169(70), 152(80), 125(100).

Withaperuvin C 4-acetate – $C_{30}H_{40}O_8$ – was obtained in the form of an amorphous powder when a solution of withaperuvin C in a mixture of acetic anhydride and pyridine was allowed to stand. ν_{max}^{KBr}, cm^{-1}: 3400, 1740, 1690, 1680, 1660, 1215. Mass spectrum, m/z (%): M^+ 510 (0.5), 468 (2.5), 450 (15), 169 (32.5), 125 (100).

Visconolide (I) – $C_{28}H_{38}O_9$, mp 232-233°C (from methanol), $[\alpha]_D^{20}$ + 119±2° (*c* 1,46; methanol), $\lambda_{max}^{C_2H_5OH}$ 220 nm (log ε 4.14); ν_{max}^{KBr}, cm^{-1}: 3400-3250, 1690, 1680. Mass spectrum, m/z (%): 500(1,5), 482(5), 464(3), 352(22), 341(21), 327(7), 315(7), 185(24), 168(100), 141(64), 123(85).

Visconolide 4,28-diacetate (II) – $C_{32}H_{42}O_{11}$ – was obtained in amorphous form by the method described above. $[\alpha]_D^{22}$ +102±2° . Mass spectrum, m/z (%): M+602(1,5), 584(6), 566(14), 542(5), 524(84), 506(70), 464(10), 446(20),383(60), 357(45), 183(70), 167(42), 141(100).

Oxidation of Visconolide (I). With ice cooling, the Jones reagent was added dropwise to a solution of 20 mg of compound (I) in 5 ml of acetone. The reaction was monitored with the aid of TLC in system 1 (with iodine as the revealing agent). After the disappearance of the initial compound from the reaction mixture, the solution was poured into water and extracted with chloroform (3 × 5 ml). The chloroform extract was washed with water and evaporated. The residue was chromatographed on a column of silica gel with elution by system 3. This gave 9 mg of crystalline 14α-hydroxy-5β,6β-epoxyandrost-2-ene-1,4,17-trione with mp 252°C (from ether), M^+ 330. On TLC, the substance obtained was identical with the product obtained on the oxidation of 4β-hydroxywithanolide E [8].

Visconolide 2,28-diacetate (II) was oxidized similarly. The products of lactone nature obtained by the oxidation of the diacetate (II) and of 28-hydroxywithaphysanolide diacetate [4] were identical on chromatographic comparison.

28-Hydroxywithaperuvin C (III) – $C_{28}H_{38}O_8$, mp 185-186°C (from methanol), $[\alpha]_D^{20}$ +152±2°, $\lambda_{max}^{C_2H_5OH}$: 228 and 317 nm (lg ε 4,02; 3,58); ν_{max}^{KBr}, cm^{-1}; 3350—3330, 1690, 1660, 1610; 1580 ; mass/spectrum, m/z (%): 484(0,5), 466(11), 343(12), 318(4), 300(11), 288(57), 185(26), 149(50), 141(100), 123(42).

28-Hydroxywithaperuvin C 6,28-diacetate (IV), $C_{32}H_{42}O_{10}$, was obtained by the method described above. Amorphous powder, $\lambda_{max}^{C_2H_5OH}$ +130±2° ; mass spectrum, m/z (%): 568(1), 526(20), 508(41), 325(21), 299(20), 286(42), 238(67), 168(100), 123(100).

SUMMARY

The epigeal part *Physalis viscosa* L. (family *Solonaceae*) has yielded minor amounts of the new withasteroids visconolide and 28-hydroxywithaperuvin C and also withaperuvin C, which has been found previously in *Physalis peruviana* L.

The PMR and ^{13}C NMR spectra of the new withasteroids have been investigated and a comparative analysis has been made of their spectral characteristics. The results have been used to establish the structure and stereochemistry of the compounds investigated. For visconolide is proposed the structure of 4β,14α,17β,20R,28-pentahydroxy-1-oxo-5β,6β-epoxy-22R-witha-2,24-dienolide and for 28-hydroxywithaperuvin C that of 6β,14α,17β,20R,28-pentahydroxy-1-oxo-22R-witha-2,4,24-trienolide.

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BIOSYNTHESIS OF ASTEROSAPONINS FROM CHOLESTEROL AND OTHER STEROLS UNDER THE CONDITIONS OF *IN VITRO* HOMOGENATES OF STARFISH GONADS AND PYLORIC CECA

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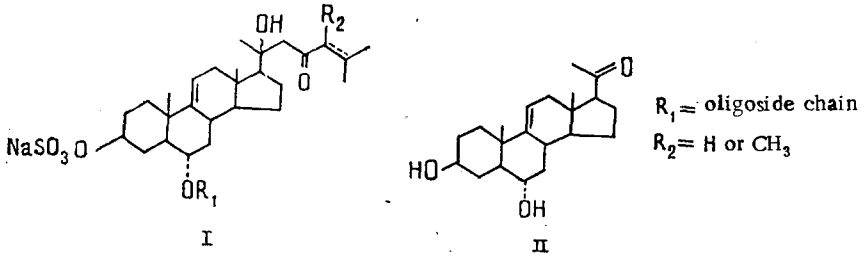
UDC: 547.918;593.92:577.121

Conditions have been selected for performing the *in vitro* biosynthesis of asterosaponins from cholesterol and other sterols in homogenates and cultures of the gonads and pyloric ceca of Far Eastern starfish. It has been shown that the aglycone moiety of an asterosaponin can be biosynthesized from cholesterol, cholesterol sulfate, 5α-cholestanol, and 3β,6α-dihydroxy-5α-cholestane but not from 3β, 6β-dihydroxy-5α-cholestane. Of the give precursors studied, cholesterol was transformed into asterosaponins most completely.

The steroid glycosides of starfish (asterosaponins) form the only group of steroid oligosides known at the present time that are biosynthesized not by higher plants but by animals. The majority of representatives of this group of compound have the general formula (I) [1-3] and on acid hydrolysis form mainly the pregnane aglycone (II) [3-6].



I II

The **biogenesis** of the asterosaponins has been little studied. Although it has been shown previously that these compounds are formed by two routes — de novo synthesis from mevalonic acid and the biotransformation of exogenous cholesterol [2] — it has remained unknown in what organs or tissues these transformations take place, whether steroid alcohols other than cholesterol are capable of acting as precursors, and what is the sequence of biosynthetic reactions leading from cholesterol to the asterosaponins. It was possible to answer these questions only by using either homogenates of individual organs or cultures of the corresponding cells or tissues.

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 663-667, September-October, 1985. Original article submitted November 1, 1984.

 0009-3130/85/2105-0622$09.50