aromatic proton resonance (1 H) could be eliminated by increasing the temperature of the sample to ca. 80 °C, indicating restricted rotation about the C(2)–C(7′) bond. ^{1}H NMR (Me$_2$SO-d_6): δ 10.713 and 10.636 (both s, 1 H, N(1)-H), 10.268 and 10.193 (both s, 1 H, N(1′)-H), 6.947 and 6.917 (both s, 1 H, C(2′)-H), in addition to the expected signals for three glutathionyl residues. The splitting of all of these signals also indicates restricted rotation about the C(2)–C(7′) bond. Assignment of the signals at δ 6.947 and 6.917 of D to C(2′)-H is based on comparisons of the chemical shifts for its precursor C, i.e., δ 6.92 and 6.89 assigned to C(2′)-H and δ 6.84 and 6.83 to C(7)-H.

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Cembrane and Pseudopterane Diterpenoids of the Octocoral *Pseudopterogorgia acerosa*

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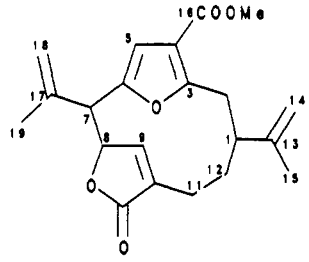
The diterpenoid metabolites isolated from *Pseudopterogorgia acerosa* collected off the coast of Tobago have been investigated. Collections made in the month of March showed a different distribution of these metabolites from a collection made in July. The dominant constituents in March were acidic diterpenoids which were converted by reaction with diazomethane to deoxypseudopterolide (1), a pseudopterane, and acerosolide (2), a cembrane. Esters 1 and 2 were isolated directly from the July collection, which also afforded the novel nitrogenous pseudopteranoid tobagolide (3). Tobagolide undergoes a novel reaction with acetic anhydride that leads to the displacement of Me$_2$N by OAc. Tobagolide reacts with diazomethane to form a pyrazoline. Structural assignments have depended heavily on 2-D NMR spectroscopy; in particular, the value of our FLOCK pulse sequence for establishing two-bond and three-bond ^{13}C–^{1}H shift correlations is illustrated.

Secondary metabolites of the gorgonian corals in the genus *Pseudopterogoria* have attracted much interest in recent years both for their chemical complexity and for their biological activity; some are of potential pharmacological value as cytotoxic or antiinflammatory agents.[1] The isolation of pseudopterolide from the Caribbean sea whip, *Pseudopterogoria acerosa*, was reported in 1982, and its remarkable structure was established.[2] It proved to be the first example of a rare group of diterpenoids having the pseudopterane skeleton incorporating a 12-membered carbocyclic framework. It has been suggested that the pseudopterane skeleton is formed biosynthetically by the rearrangement of a precursor with the cembrane skeleton that incorporates a 14-membered carbocyclic ring. Cembranoids are common in other gorgonian genera, but their occurrence in the genus *Pseudopterogoria* appears to be limited to very few species.[1]

We have investigated the constituents of *P. acerosa*, which occurs abundantly on reefs off the coast of Tobago, and we report here on the isolation and structure elucidation of three new metabolites of this species. Collections made in the month of March (1984 and 1985) provided two acidic diterpenes, a pseudopteranoid and a cembranoid, which were converted by treatment with diazomethane to their methyl esters, deoxypseudopterolide (1) and acerosolide (2), to facilitate isolation. A collection made in the month of July (1987) had a completely different distribution of metabolites; the principal constituent was the novel nitrogenous pseudopteranoid tobagolide (3), which we have described in a preliminary communication.[3] Small amounts of deoxypseudopterolide and acerosolide were isolated directly (i.e., without diazomethane treatment) from the July specimen.



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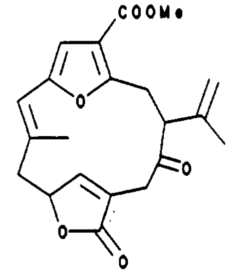

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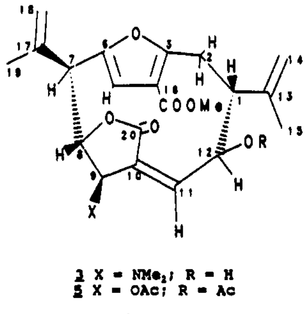

3 X = NMe$_2$; R = H
5 X = OAc; R = Ac

Tobagolide was isolated from the extract (without the use of diazomethane) as white crystals, mp 165–166 °C, $[\alpha]_D$ –135°, and the formula $C_{23}H_{29}O_6N$ was established by HRMS. The spectroscopic characteristics of tobagolide, collected in a routine manner, indicated that it had an

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(1) Fenical, W. *J. Nat. Prod.* 1987, *50*, 1001.
(2) Bandurraga, M. M.; Fenical, W.; Donovan, S. F.; Clardy, J. *J. Am. Chem. Soc.* 1982, *104*, 6463.
(3) Tinto, W. F.; Chan, W. R.; Reynolds, W. F.; McLean, S. *Tetrahedron Lett.* 1990, *31*, 465.

0022-3263/91/1956-1773$02.50/0

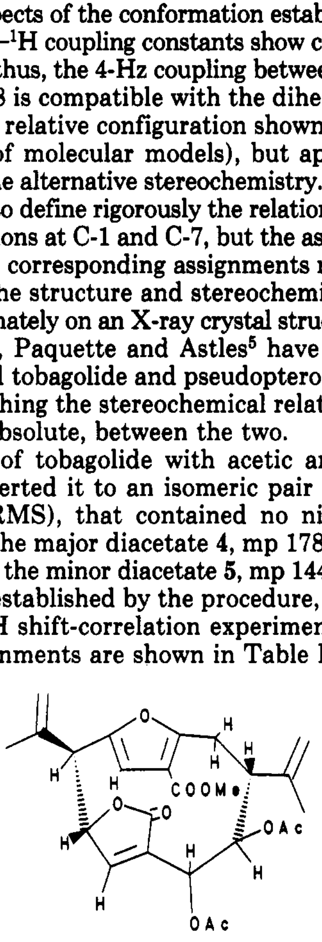
Table I. NMR Characteristics of Tobagolide (3)[a]

position	δ_C	δ_H (J_{HH})	obsd 2- or 3-bond connectivity	NOE obsd
1	49.50	3.58 (12.9, 10.3, 3.0)	5.01, 4.97, 3.61, 2.66, 1.83_5	
2	29.48	2.66 (15.6, 3.0) 3.61 (15.6, 12.9)	4.01, 3.58	
3	160.30	-	6.40, 3.61, 2.66	
4	115.93	-	6.40, 2.66	
5	112.28	6.40 (-)	3.57 (w)	
6	150.80	-	6.40, 5.06, 3.57 (w)	
7	49.21	3.57 (4.0, 1.8, 1.8, 0.9q)	5.09, 5.06 (w), 4.92, 3.01, 1.96_5	
8	84.34	5.06 (4.0, ~0.5)	3.57	
9	68.93	3.01 (~0.5, ~0.5)	5.94, 5.06 (w), 2.20_5	5 (6), 7 (6), 8 (1), 11 (9)
10	130.08	-	5.94 (w), 5.06 (w), 4.01 (w), 3.01	
11	143.92	5.94 (7.2, ~0.5)	4.01 (w), 3.01	9 (8), 12 (13)
12	70.00	4.01 (12.5, 10.3, 7.2)	5.94, 3.58 (w), 2.66 (w)	
13	145.36	-	5.01 (w), 4.97 (w), 3.58 (w), 1.83_5	
14	113.38	c4.97_t (1.8, 1.8q) t5.00_t (1.8, 0.9q)	3.58 (w), 1.83_5	
15	18.76	1.83_5 (1.8, 0.9)	5.01, 4.97, 3.58 (w)	12 (t), 14c (5)
16	163.79	-	5.94, 5.06 (w), 3.01	
17	139.55	-	5.06 (w), 4.92 (w), 3.57, 1.96_5	
18	115.87	c4.92 (1.8, 1.8, 1.8q) t5.09 (1.8, 1.8, 0.9q)	3.57 (w), 1.96_5	
19	22.02	1.96_5 (1.8, 0.9, 0.9)	5.09, 4.92	5 (3), 7 (4), 8 (7), 18c (5)
20	171.63	-	5.94, 5.06 (w), 3.01	
$\mathrm{COO\underline{CH}_3}$	51.64	3.85 (-)	-	
$\mathrm{N(\underline{CH}_3)_2}$	41.36	2.20_5 (-)	3.01, 2.20_5	9 (23), 11 (7), 8 (20)
$\mathrm{O\underline{H}}$	-	4.58 (12.5)	-	

[a] Data are for solutions in $CDCl_3$. Chemical shifts were measured at 100.6 MHz for ^{13}C and 400 MHz for ^1H. Coupling constants (J_{HH}, Hz) are for coupling to single protons unless labeled q (quartet splitting). Olefinic protons labeled c and t are cis and trans, respectively, to the vicinal Me. Connectivity data are for cross peaks observed at δ_C in column 2 and δ_H values listed; weak peaks are shown (w). NOE data are enhancements (%) observed at ^1H at position listed on irradiation at δ_H in column 3.

unusual structure, so a series of 2-D NMR experiments was carried out. From ^1H-COSY-45 and one-bond ^{13}C-^1H shift-correlation experiments, all carbons and their attached hydrogens were identified. An *n*-bond ($n = 2$ or 3) ^{13}C–^1H shift-correlation experiment was then carried out using our FLOCK pulse sequence.[4] The results, shown in Table I, clearly establish the structure shown in **3** for tobagolide. Of the 68 possible two- or three-bond connectivities, 57 are observed, and eight of those unobserved are three-bond connectivities with angular dispositions that should lead to very small coupling constants (and no cross peak) if the stereochemistry is that shown. This impressive array of connectivities is more than sufficient to define the structure unequivocally because most structural units can be traced in several different ways, and it illustrates one valuable aspect of the FLOCK pulse sequence. A second major advantage of FLOCK over earlier ^{13}C-detected sequences lies in its total suppression of cross peaks from one-bond connectivities that can seriously complicate assignments in complex molecules with many two- and three-bond connectivities.[4] A specific example in the present case provides an illustration: the cross peak between the methyl carbon at δ 41.4 and the methyl proton singlet at δ 2.21 is due to a three-bond coupling, not a one-bond coupling, allowing the signals to be assigned to the NMe_2 moiety. The stereochemistry of **3** was determined from measured coupling constants and from several 1-D NOE experiments; Table I lists the data. The NOE results show interatomic relationships in the macrocyclic ring that reveal aspects of the conformation and shape of the molecule. In particular, the observation of a significant (6%) positive NOE for H-5 on irradiation of H-9 (and the corresponding absence of an NOE effect for H-5 on irradiation of the NMe_2 protons) indicates that **3** adopts a "clamshell" shape with clearly defined "inside" and "outside" regions; as a consequence, the two faces of even planar segments have distinctly different environments. With these aspects of the conformation established, vicinal ^1H–^1H and ^{13}C–^1H coupling constants show configurational relationships; thus, the 4-Hz coupling between the protons at C-7 and C-8 is compatible with the dihedral angle expected for the relative configuration shown (based on an examination of molecular models), but appears incompatible with the alternative stereochemistry. Our data are not sufficient to define rigorously the relationship between the configurations at C-1 and C-7, but the assignments are in accord with corresponding assignments made to pseudopterolide, the structure and stereochemistry of which are based ultimately on an X-ray crystal structure analysis. Very recently, Paquette and Astles[5] have synthetically interconverted tobagolide and pseudopterolide, unequivocally establishing the stereochemical relationship, both relative and absolute, between the two.

Treatment of tobagolide with acetic anhydride and pyridine converted it to an isomeric pair of diacetates, $C_{25}H_{28}O_9$ (HRMS), that contained no nitrogen. The structures of the major diacetate **4**, mp 178–179 °C, $[\alpha]_D$ +88.9°, and of the minor diacetate **5**, mp 144–145 °C, $[\alpha]_D$ +10.9°, were established by the procedure, including the *n*-bond ^{13}C–^1H shift-correlation experiment, used for **3**. Spectral assignments are shown in Table II.



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[4] Reynolds, W. F.; McLean, S.; Perpick-Dumont, M.; Enriquez, R. G. *Magn. Reson. Chem.* **1989**, *27*, 162.

[5] Leo A. Paquette, personal communication.

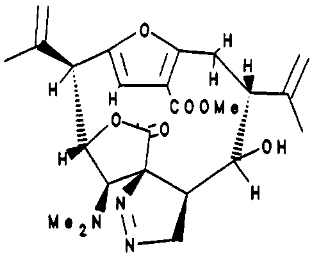
Table II. Assigned ^1H and ^{13}C Spectral Data for 4–6[a]

	4		5		6	
position	δ_C	δ_H (J_{HH})	δ_C	δ_H (J_{HH})	δ_C	δ_H (J_{HH})
1	42.99	3.32 (12.7, 3.4, 1.4)	46.51	3.96 (12.7, 11.3, 4.6)	45.31	3.21 (11.0, 11.0, 3.6)[b]
2	31.09	2.96 (15.3, 3.4) 3.57 (15.3, 12.7)	28.82	2.67 (15.4, 4.6) 3.67 (15.4, 12.7)	30.48	2.89 (15.0, 3.6) 3.19 (15.0, 11.0)
3	160.28	–	159.95	–	159.1	–
4	115.04	–	116.99	–	114.00	–
5	110.58	6.41	112.17	6.47	111.12	6.52
6	150.17	–	150.58	–	150.22	–
7	48.35	3.84 (3.6, 1.8, 1.8)[c]	47.70	3.73 (3.9, 1.8, 1.8)[c]	50.30	3.55 (2.4)
8	80.25	5.41 (3.6, 1.7, 0.7)	83.63	4.94 (11.3, 7.5)	79.92	5.17 (3.7, 2.4)
9	149.95	7.12 (1.7, 0.7)	75.93	4.99 (11.3, 7.5)	74.92	2.92 (3.7)
10	130.53	–	128.37	–	92.88	–
11	72.48	5.56 (2.4, 0.7, 0.7)	137.85	5.94 (7.5, 0.6)	51.35	1.23 (7.1, 1.1)
12	76.74	4.64 (2.4, 1.4)	70.08	4.99 (11.3, 7.5)	77.16	3.20 (11.0)
13	143.62	–	144.10	–	145.68	–
14	115.04	c5.04 (1.8)[d] t5.07_5 (1.8)	113.95	c4.95_5 (1.8)[d] t5.01 (1.8)	113.41	c4.80 (1.80)[d] t4.84 (1.8)
15	22.69	1.92_5 (1.8, 0.9)	19.61	1.78 (1.8, 0.9)	18.36	1.68 (1.8, 0.9)
16	163.85	–	163.54	–	163.68	–
17	140.90	–	138.99	–	141.31	–
18	115.55	c4.94 (1.8, 1.8)[d] t5.09 (1.8, 1.8)	116.03	c4.93 (1.8, 1.8)[d] t5.09 (1.8, 1.8)	115.71	c4.82 (1.8)[d] t5.06 (1.8)
19	21.70	1.96 (1.8, 0.9, 0.9)	21.99	1.92 (1.8, 0.9, 0.9)	21.55	1.93 (1.8, 0.9)
20	170.12	–	166.25	–	176.91	–
21	51.33	3.81	51.77	3.86	51.65	3.80
22	–	–	–	–	82.30	4.18 (17.1, 7.1) 4.85 (17.1, 1.1)
NMe_2	–	–	–	–	42.34	2.28
acetate signals						
	170.33	– (at C-12)	170.34	– (at C-12)	–	–
	21.00	2.04_5	20.98	2.06	–	–
	170.90	– (at C-11)	170.53	– (at C-9)	–	–
	20.64	2.14	20.68	2.02	–	–

[a] See Table I for conditions employed and the meaning of symbols used. [b] Coupling constants for 6 were determined from the spectrum of a C_6D_6 solution. [c] A further quartet splitting of ca. 0.9 Hz by C-19 Me protons was also observed. [d] Cis protons show a further quartet splitting of ca. 1.8 Hz by Me protons. Trans protons show a further quartet splitting of ca. 0.9 Hz by Me protons.

The replacement of NMe_2 by OAc is a reaction for which we have found no precedent. It is reasonable to suppose that the nitrogen in 3 reacts with acetic anhydride to form a strained allylic *N*-acetylammonium species that readily eliminates the acetamide moiety to form an allylic cation that can react with acetate ions at either C-9 or C-11. The reaction is completely stereoselective at both sites because approach of acetate to the rigid allylic cation is possible only from outside the "clamshell".

Tobagolide reacted readily with diazomethane to form a pyrazoline, the structure of which was established as 6 by methods similar to those used for 3 to 5; the data are summarized in Table II.



6

Deoxypseudopterolide (1), $C_{21}H_{24}O_5$, was obtained as prisms, mp 139–140 °C, $[\alpha]_D$ + 62°, and acerosolide (2), $C_{21}H_{22}O_6$, was obtained as a gum, $[\alpha]_D$ +35°. In both cases, the IR spectra revealed the nature of the carbonyl functions present; the ^{13}C NMR spectra showed resolved signals for all of the carbons present, and the major features of the ^1H NMR spectra could be reasonably assigned with the help of spin–spin decoupling and COSY experiments. A comparison of the NMR spectral data for 1 with those for 4, assigned above, provides confirmation for the assignment of its structure; the stereochemistry of 1 probably corresponds with that of 4 at relevant centers since J_{HH} values around these centers are similar in the two compounds. In the case of 2, the UV spectrum (λ_{max} 253 nm) showed the presence of extra conjugation, and the IR spectrum (1710 cm^{-1}) revealed a saturated ketone. The NMR data could be rationalized by assigning acerosolide a cembranoid structure, and comparison with the data published for related cembranoids[6] provides confirmation for this assignment. The stereochemistry at the 7,8 double bond is indicated by the absence of an observed NOE effect at the vinyl proton (δ 5.93) when the C-19 protons (δ 1.56) were irradiated.

It follows that *P. acerosa* biosynthesizes both pseudopteranoids and cembranoids. These two classes of diterpenes have previously been found together in the soft coral *Gersemia rubiformis*.[5]

Experimental Section

Specimens of *P. acerosa* were collected during the months of March (1984 and 1985) and July (1987) from reefs at depths between 6 and 10 m at locations (Man-of-War Bay, Tyrrel's Bay, and Culloden Bay) on the north coast of Tobago. Voucher specimens were lodged at the Institute of Marine Affairs, Chaguaramas. Specimens were immersed in acetone from storage during collection. Material for extraction was placed in fresh acetone, macerated, and allowed to stand for 1 day. The suspension was filtered, and the filtrate was concentrated under

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(6) Williams, D.; Andersen, R. J.; Van Duyne, G. D.; Clardy, J. *J. Org. Chem.* 1987, *52*, 332.

reduced pressure. Two isolation procedures were then employed.

(i) Material obtained from March collections was diluted with methanol to produce a suspension in 10% methanol in water and extracted with petroleum ether (bp 60–80 °C) and then chloroform. The chloroform extract afforded a dark red gum (7.3 g, corresponding to 3.7% of the weight of dried specimen), which was chromatographed on silica gel. Elution with 3:1 ethyl acetate/petroleum ether gave an acidic fraction (844 mg), which was treated with an excess of diazomethane in ether. Preparative layer chromatography of the product provided deoxypseudopterolide (97 mg) and acerosolide (32 mg).

(ii) Material obtained from July collections was exhaustively extracted with dichloromethane. Material (210 g, corresponding to 21% of the weight of dried specimen) obtained from this extract was dissolved in 300 mL of 9:1 methanol/water and exhaustively extracted with petroleum ether. The methanolic solution was then diluted with 200 mL of water and extracted with dichloromethane. The dichloromethane extract afforded a dark viscous oil (80 g), which was flash chromatographed on silica gel with solvents of increasing polarity. Fractions eluted with petroleum ether/acetone mixtures provided material (19.6 g) that was chromatographed on silica gel with benzene as solvent. Purification by HPLC provided deoxypseudopterolide (260 mg) and acerosolide (371 mg). Fractions eluted with ethyl acetate gave material that was rechromatographed on silica gel with 4:1 petroleum ether/acetone as solvent to provide material (3 g), from which pure tobagolide (523 mg) was obtained by recrystallization from petroleum ether/acetone.

Deoxypseudopterolide (1). Recrystallization of 1 from petroleum ether/acetone provided white prisms: mp 139–140 °C; $[\alpha]_D$ +62° (*c* 0.23, $CHCl_3$); IR ($CHCl_3$) 3080, 1760, 1720, 1640; UV 245 (6000); ^1H NMR (360 MHz) 0.84 (ddd, J = 14, 3, 3 Hz, 1 H), 1.80 (m, 1 H), 1.81 (m, 3 H), 1.99 (m, 3 H), 2.21 (d, J = 14 Hz, 1 H), 2.44 (ddd, J = 14, 14, 3 Hz, 1 H), 2.73 (m, 1 H), 2.78 (d, J = 16 Hz, 1 H), 3.32 (dd, J = 16, 12 Hz, 1 H), 3.83 (s, 3 H), 3.84 (d, J = 4 Hz, 1 H), 4.82 (m, 1 H), 4.86 (m, 1 H), 5.05 (m, 1 H), 5.07 (m, 1 H), 5.44 (d, J = 4 Hz, 1 H), 6.39 (m, 1 H), 6.75 (m, 1 H); ^{13}C NMR (20 MHz) 19.2 (3), 21.6 (3), 22.8 (2), 31.5 (2), 35.1 (2), 41.6 (1), 48.5 (1), 51.2 (3), 80.6 (1), 109.9 (1), 111.2 (2), 114.8 (2), 115.3 (0), 137.1 (0), 141.3 (0), 146.8 (1), 147.3 (0), 150.5 (0), 161.6 (0), 164.1 (0), 175.1 (0); MS 206 (56), 188 (19), 177 (5), 163 (14), 161 (14), 151 (64), 135 (15), 122 (5), 115 (11), 105 (5), 91 (100); CIMS 374 ($[M + NH_4]^+$).

Acerosolide (2). This compound could be purified by chromatography and obtained as a gum that appeared to be homogeneous but to undergo a slow degradation on storage: $[\alpha]_D$ +35 ° (*c* 0.43, $CHCl_3$); IR ($CHCl_3$) 3080, 3020, 1760, 1715, 1710, 1640; UV 253 (6800); ^1H NMR (400 MHz) 1.56 (d, J = 1.5 Hz, 3 H), 1.79 (m, 3 H), 2.46 (dd, J = 14, 3 Hz, 1 H), 2.93 (dd, J = 14, 4 Hz, 1 H), 3.03 (d, J = 12 Hz, 1 H), 3.19 (dd, J = 16, 3 Hz, 1 H), 3.52 (dd, J = 16, 12 Hz, 1 H), 3.81 (s, 3 H), 3.91 (d, J = 12 Hz, 1 H), 4.07 (d, J = 12 Hz, 1 H), 5.08 (m, 2 H), 5.26 (m, 1 H), 5.93 (m, 1 H), 6.31 (m, 1 H), 7.31 (m, 1 H); ^{13}C NMR (20 MHz) 20.2 (3), 22.0 (3), 28.3 (2), 37.6 (2), 40.1 (2), 51.3 (3), 58.6 (1), 78.9 (1), 107.9 (1), 113.8 (0), 116.5 (2), 119.8 (1), 127.9 (0), 139.4 (0), 140.3 (0), 148.8 (0), 149.5 (1), 158.4 (0), 164.2 (0), 173.3 (0), 203.5 (0); MS 370 (21), 339 (7), 246 (37), 245 (16), 192 (68), 191 (70), 187 (16), 186 (15), 133 (65), 104 (24), 43 (100); exact mass 370.1447, calcd for $C_{21}H_{22}O_6$ 370.1416.

Tobagolide (3). Pure material was obtained as colorless prisms: mp 165–166 °C, $[\alpha]_D$ −130.5° (*c* 0.22, $CHCl_3$), IR (KBr) 1723, 1718, 1644; UV 272 (2940), 233 (shoulder, 6550), end absorption; MS 415 (25), 386 (22), 384 (18), 372 (20), 371 (46), 370 (23), 354 (16), 339 (37), 272 (18), 247 (51), 246 (97), 245 (80), 215 (25), 214 (24), 213 (23), 195 (23), 194 (100), 193 (44), 170 (23), 166 (21), 139 (42); exact mass 415.1998, calcd for $C_{23}H_{29}O_6N$ 415.1995. Treatment of **3** (350 mg) with acetic anhydride and pyridine at room temperature overnight led to two diacetates, which were separated by chromatography. The **major diacetate 4** (175 mg) was obtained as crystals: mp 178–179 °C; $[\alpha]_D$ +88.9° (*c* 0.22, $CHCl_3$); IR (KBr) 1754, 1748, 1712; UV 244 (shoulder, 5100), end absorption; MS 472 (18), 441 (11), 413 (18), 412 (33), 353 (18), 352 (40), 321 (38), 320 (95), 293 (35), 292 (48), 270 (19), 269 (53), 246 (24), 245 (63), 193 (33), 192 (82), 191 (100), 133 (61), 132 (25); exact mass 472.1684, calcd for $C_{25}H_{28}O_9$ 472.1733. The **minor diacetate 5** (52 mg) was obtained as crystals: mp 144–145 °C; $[\alpha]_D$ +10.9° (*c* 0.2, $CHCl_3$); MS 472 (65), 413 (33), 412 (31), 353 (18), 352 (27), 321 (22), 320 (29), 293 (21), 292 (24), 289 (25), 247 (32), 246 (29), 235 (46), 215 (36), 193 (100), 192 (63), 191 (38), 133 (42); exact mass 472.1685, calcd for $C_{25}H_{28}O_9$ 472.1733.

Treatment of **3** (81 mg) with an excess of diazomethane in ether overnight followed by preparative TLC converted it to the **pyrazoline 6** (50 mg): mp 159–161 °C; UV 316 (320), 249 (5000), 219 (6200); MS 457 (8), 430 (31), 429 (70), 401 (21), 400 (50), 398 (25), 397 (36), 372 (20), 368 (15), 248 (24), 247 (68), 246 (81), 245 (34), 208 (50), 182 (56), 170 (45), 154 (50), 153 (49), 124 (40), 86 (100); exact mass 457.2199, calcd for $C_{24}H_{31}O_6N_3$ 457.2207.

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Supplementary Material Available: Copies of ^1H NMR spectra for 1 and 3–6, ^{13}C NMR spectra for 1–6, and mass spectra for 1 (13 pages). Ordering information is given on any current masthead page.