6.89. Found: C, 76.75; H, 8.18; N, 7.31.

A picrate was prepared in chloroform and crystallized from 90% ethanol; mp 248–250 °C. Anal. Calcd for $C_{19}H_{20}O_8N_4$: C, 52.78; H, 4.66; N, 12.96. Found: C, 52.80; H, 4.58; N, 12.95.

Acknowledgment. We thank Professor A. Hagedorn and S. Grenci for helpful comments and technical assistance.

Registry No. **1a**, 81523-31-1; **1b**, 85507-37-5; **1c**, 22568-03-2; **1d**, 85507-38-6; **1e**, 85507-39-7; **1f**, 85507-40-0; **2**, 42392-37-0; **3a**, 69649-19-0; **3a** 2,4-dinitrophenylhydrazone, 69649-20-3; **3b**, 58228-93-6; **3c**, 69649-13-4; **3d**, 2958-72-7; **3e**, 85507-41-1; **3g**, 85507-42-2; **3g** picrate, 85610-83-9; **3h**, 85507-43-3; **4**, 85507-44-4; **5**, 85507-45-5; **7**, 85507-46-6; **8**, 85507-47-7; trimethyl orthoformate, 149-73-5; benzyl mercaptan, 100-53-8; potassium phthalimide, 1074-82-4; *p*-bromobenzenesulfonyl chloride, 98-58-8.

Sesquiterpenoid Constituents of Eight Porostome Nudibranchs

Roy K. Okuda and Paul J. Scheuer*

Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822

Jill E. Hochlowski, Roger P. Walker, and D. John Faulkner*

Scripps Institution of Oceanography, La Jolla, California 92093

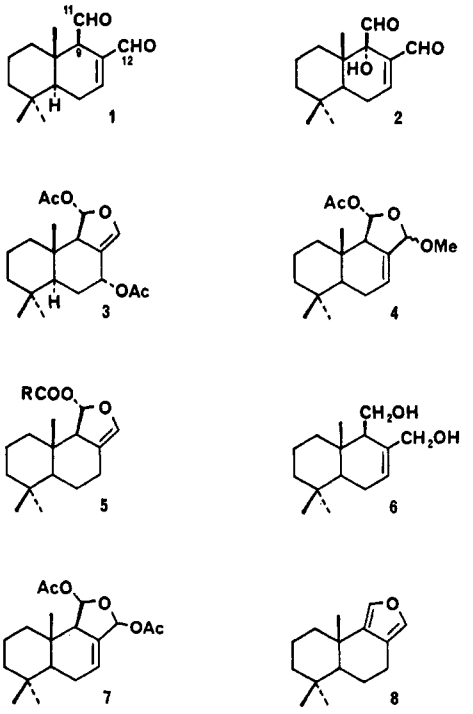
Received October 18, 1982

Sesquiterpenes of the drimane series were isolated from eight porostome nudibranchs. A mixture of polygodial (1) and olepupuane (3), a new sesquiterpene diacetate, was obtained from *Dendrodoris nigra*, *Dendrodoris tuberculosa*, and *Dendrodoris krebsii*. Olepupuane (3) and the sesquiterpene esters 5 were found in *Doriopsilla albopunctata*, *Doriopsilla janaina*, and an undescribed yellow porostome, although one collection of *Doriopsilla albopunctata* contained only olepupuane (3) while a second collection contained a related methoxy acetal 4. Two undescribed porostomes contained only the sesquiterpene esters 5 found previously in *Dendrodoris limbata*. The structures of olepupuane (3) and the methoxy acetal 4 are based on interpretation of spectral data.

The porostome nudibranchs, of which the genera *Dendrodoris* and *Doriopsilla* are examples, are a group of dorid nudibranchs distinguished by the absence of a radula. Like other dorid nudibranchs,[1] the porostomes appear to employ a chemical defense mechanism. The chemicals implicated in their defense are all sesquiterpenes of the drimane series and are closely related to the known insect antifeedants polygodial (1) and warburganal (2) (Chart I), first isolated from a number of terrestrial plants.[2] We now report the structural elucidations of the noval sesquiterpenes olepupuane (3) and the methoxy acetal 4 and several new sources of polygodial (1) and the mixed sesquiterpene esters 5, previously found in *Dendrodoris limbata*.[3,4]

Specimens of *Dendrodoris nigra* were collected at Ala Moana reef, at Fort Kamehameha, and at Pupukea, all on Oahu; *Dendrodoris tuberculosa* were found at Ala Moana and at Pupukea; *Dendrodoris krebsii* were obtained from Bahia de los Angeles, Baja California, Mexico. Collections of *Doriopsilla albopunctata* were made at La Jolla, CA, Sunset Cliffs, San Diego, CA and Bahia de los Angeles. *Doriopsilla janaina*, the "gulf yellow porostome",[5] the "giant brown porostome", and "Fay's porostome" were all collected at Bahia de los Angeles. *D. nigra* and *D. tuberculosa* were extracted by immersion in distilled hexane for 5–10 min and then transferred to fresh solvent for 1–2 days. In all cases the initial extract contained the sesquiterpenes of interest while the second extract contained largely fats, sterols, and pigments in addition to smaller quantities of sesquiterpenes. The specimens of *Doriopsilla albopunctata* from San Diego and La Jolla were extracted with cold methanol (−20 °C) while all other specimens were extracted with cold acetone for the length of time required to return the samples to the laboratory (1–3 weeks). In every case the sesquiterpenes were easily purified by

Chart I



(1) Schulte, G. R.; Scheuer, P. J. *Tetrahedron* **1982**, *38*, 1857. Thompson, J. E.; Walker, R. P.; Wratten, S. J.; Faulkner, D. J. *Ibid* **1982**, *38*, 1865.

(2) Nakanishi, K.; Kubo, I. *Isr. J. Chem.* **1977**, *16*, 28.

(3) Cimino, G.; De Rose, S.; De Stefano, S.; Sodano, G. *Tetrahedron Lett.* **1981**, *22*, 1271.

(4) Cimino, G.; De Rosa, S.; De Stefano, S.; Sodano, G. *Comp. Biochem. Physiol. B* **1982**, *73B*, 471. D'Ischia, M.; Prota, G.; Sodano, G. *Tetrahedron Lett.* **1982**, *23*, 3295.

(5) The trivial names employed in this paper allow biologists who are familiar with Gulf of California fauna to identify these animals prior to their formal description.

0022-3263/83/1948-1866$01.50/0

Table I. Metabolites from Porostome Nudibranchs[a]

animal	polygodial (1)	olepupuane (3)	methoxy acetal 4	esters 5
Dendrodoris nigra	0.1	0.1		
Dendrodoris tuberculosa	3.5	3.8		
Dendrodoris krebsii	0.2	0.2		9
Dendrodoris limbata[3]	3.9			
Doriopsilla albopunctata				
La Jolla, CA		0.07		
Sunset Cliffs, CA			0.05	
Baja California		0.1		0.1
Doriopsilla janaina		0.15		0.15
"gulf yellow porostome"		0.15		0.4
"giant brown porostome"				2.7
"Fay's porostome"				3.8

[a] The values given are the weight (in milligrams) per animal.

HPLC on Lichrosorb Si-60 or Partisil although some decomposition occurred during purification. The sesquiterpenes isolated by these methods are shown in Table I.

Polygodial (1) was identified by comparison of its physical properties with those previously reported.[6-8] Distinction of polygodial from 9-epipolygodial was made possible by comparing the aldehydic ^{1}H NMR spectral data [δ ($CDCl_3$) 9.54 (d, 1 H, J = 4.4 Hz), 9.46 (s, 1 H)] with those of polygodial[9] [δ ($CDCl_3$) 9.56 (d, 1 H, J = 5 Hz), 9.47 (s, 1 H)] and 9-epipolygodial[10] [δ (CCl_4) 9.94 (d, 1 H, J = 2 Hz), 9.43 (s, 1 H)].

The second metabolite, olepupuane (3), had the molecular formula $C_{19}H_{28}O_5$. The successive losses of acetic acid and of ketene from the molecular ion in the mass spectrum together with ^{1}H NMR signals at δ 2.04 (s, 3 H) and 2.07 (s, 3H) indicated that olepupuane (3) was a sesquiterpene diacetate. The drimane skeleton was established by acid-catalyzed hydrolysis of olepupuane (3) to polygodial (1) and by reduction of olepupuane (3) with lithium aluminum hydride in tetrahydrofuran to the diol 6 that had spectral data identical with those of a synthetic sample.[12] On consideration of only these reactions, the most plausible structure for the diacetate was the α,α'-diacetoxytetrahydrofuran 7. However, comparison of the coupling constants of the protons at C-11 and C-12 in the ^{1}H NMR spectrum of olepupuane with those of heteronemin[13] and the ^{13}C NMR signals at δ 98.7 and 65.8, assigned to the carbons at C-11 and C-7, respectively, suggested the isomeric structure 3 for oleupupane. The ^{1}H NMR spectrum of olepupuane (3) in either carbon tetrachloride or deuteriochloroform contained overlapping acetal and olefinic signals that could be conveniently separated in deuteriobenzene solution. The acetal proton signal at δ 6.70 (d, 1 H, J = 2.3 Hz) was coupled to the methine proton signal at δ 2.73 (m, 1 H) and showed a strong nuclear Overhauser effect to the bridgehead methyl group signal at δ 0.55 (s, 3 H), indicating that the acetal proton at C-11 was trans to the axial proton at C-9. The olefinic proton signal at δ 6.13 (d, 1 H, J = 1.8 Hz) was allylically coupled to the axial proton signal at δ 2.73 (m, 1 H) and showed a strong nuclear Overhauser effect to the equatorial α-acetoxy proton signal at δ 5.65 (m, 1 H, J = 3.5, 2.0 Hz, C-7). Since olepupuane (3) must have a trans decalin ring system to permit its conversion into polygodial (1) and diol 6, the relative stereochemistry was established at all asymmetric centers.

One collection of *Doriopsilla albopunctata* that was extracted with cold methanol contained the methoxy acetal 4, presumably obtained by allylic methanolysis of olepupuane (3).[14] The methoxy acetal 4 had the molecular formula $C_{18}H_{28}O_4$. The ^{1}H NMR spectrum contained acetal proton signals at δ 6.15 (d, 1 H, J = Hz, C-11) and 4.96 (s, 1 H, C-12), a methoxy signal at δ 3.16 (s, 3 H), and an acetoxy signal at δ 2.01 (s, 3 H). The C-9 axial proton signal at δ 2.48 (m, 1 H, J = 4, 3, 3 Hz) exhibited vicinal coupling to the C-11 proton signal, allylic coupling to the olefinic proton signal at δ 5.69 (m, 1 H, J = 3, 3, 3 Hz), and homoallylic coupling to the C-6 axial proton signal at δ 1.92 (m, 1 H, J = 18, 12, 3, 3 Hz) that was in turn coupled to the C-6 equatorial proton signal at δ 1.35 (dd, 1 H, J = 12, 5 Hz). The methoxy acetal 4 was also reduced to diol 6 by using lithium aluminum hydride in tetrahydrofuran.

The sesquiterpene esters 5 had spectral data almost identical with those reported from the Mediterranean porostome *Dendrodoris limbata*. The configuration at C-11 of the sesquiterpene esters was determined by observation of a nuclear Overhauser effect between signals at δ 0.81 (s, 3 H) and 6.31 (d, 1 H, J = 2 Hz) in the ^{1}H NMR spectrum. The esters were subjected to an acid-catalyzed elimination reaction to give euryfuran (8)[15] and mixtures of C_{14}–C_{20} fatty acids that were converted into the corresponding methyl esters and analyzed by gas chromatography.

Polygodial (1) had originally been identified as an insect antifeedant and has recently been reported as a fish antifeedant.[4] Olepupuane (3) was shown to inhibit feeding of the Pacific damsel fish (*Dascyllus aruanus*) on food pellets that were impregnated with various concentrations (5–50 μg/mg) of olepupuane (3). The ED_{50} of olepupuane (3) was found to be 15–20 μg/mg of pellet, comparable to that of polygodial (1).[4] Using the same assay, the sesquiterpene esters 5 did not inhibit feeding at 100 μg/mg.

Dendrodoris nigra is known to feed on the sponge *Suberites* sp.[16] We have not been able to find this sponge at our collection sites in Hawaii. At Bahia de los Angeles, several porostomes were observed feeding on *Pseudo-*

(6) Ohsuka, A. *Nippon Kagaku Zasshi* **1962**, *83*, 757; *Chem. Abstr.* **1963**, *59*, 6444.
(7) Barnes, C. S.; Loder, J. W. *Aust. J. Chem.* **1962**, *15*, 322.
(8) Kubo, I.; Lee, Y.-W.; Pettei, M.; Pilkiewicz, F.; Nakanishi, K. *J. Chem. Soc., Chem. Commun.* **1976**, 1013.
(9) Aasen, A. J.; Nishida, T.; Enzell, C. R.; Appel, H. H. *Acta Chem. Scand., Ser. B* **1977**, *B31*, 51.
(10) Ohsuka, A.; Matsukawa, A. *Chem. Lett.* **1979**, 635.
(11) Olepupa is the Hawaiian for shell-less.
(12) Howell, S. C.; Ley, S. V.; Mahon, M.; Worthington, P. A. *J. Chem. Soc., Chem. Commun.* **1981**, 507. We thank Professor Ley for spectra of diol 6.
(13) Yasuda, F.; Tada, H. *Experienta* **1981**, *37*, 110.
(14) It is interesting to note that the methoxy acetal 4 was found only in the collection of animals that were stored in methanol for the least time.
(15) Hochlowski, J. E.; Walker, R. P.; Ireland, C.; Faulkner, D. J. *J. Org. Chem.* **1982**, *47*, 88.
(16) Young, D. K. Ph.D. Thesis, University of Hawaii, 1966.

suberites pseudos Dickinson but neither this sponge nor any other that we collected in the Gulf of California contained drimane sesquiterpenes.

Experimental Section

Optical rotations were measured on a Bendix Ericsson ETL-NPL or a Perkin-Elmer Model 141 polarimeter. Mass spectra were recorded on Varian MAT-311, Finnigan 105, and Hewlett-Packard 5930A mass spectrometers. NMR spectra were determined on Varian XL-100, Nicolet NT-300, Bruker WH-500, Nicolet Wide-bore 200-MHz, and custom-built Oxford/Nicolet 360 MHz instruments. Infrared spectra were measured on Perkin-Elmer 467 or 137 spectrophotometers. Ultraviolet spectra were recorded on Cary 14, Beckman ACTA, C111, and Varian Cary 219 spectrophotometers.

Collection and Isolation Procedures. Specimens of *Dendrodoris nigra* and *D. tuberculosa*, collected by snorkeling at -0.5 to -2 m at various locations on Oahu, were immersed intact in redistilled hexanes for 5–10 min. The extract was concentrated in vacuo to a yellowish oil, typically 0.03% by weight of live nudibranch. Chromatography of this oil by LC on μ-Lichrosorb Si-60 (Unimetrico-Knauer) with 7:3 hexanes/ethyl acetate as the eluant afforded pure polygodial (1) and olepupuane (3) in a 1:1 ratio (see Table I).

Four specimens of *Dendrodoris krebsii* (82-079) were collected at Bahia de los Angeles, Baja California, in April 1982. The animals (0.8 g dry weight) were stored in acetone (15 mL) at 0 °C for 2 weeks. The acetone was decanted and the solvent evaporated to yield an aqueous suspension that was partitioned between water (10 mL) and dichloromethane (2 × 20 mL). The combined dichloromethane extracts were dried over sodium sulfate, and the solvent was evaporated to yield an oil. A solution of the oil in ether was filtered through a silica gel plug and the nonpolar material separated by LC on μ-Porasil by using ether as the eluant to give fats, sterols, and two sesquiterpenes, polygodial (1; 0.8 mg, 0.2 mg/animal, 0.1% dry weight) and olepupuane (3; 0.8 mg, 0.2 mg/animal, 0.1% dry weight).

Thirty specimens of *Doriopsilla albopunctata* (average length 7 mm) were collected from rock pools at low tide in July 1980 at South Bird Rock, La Jolla, CA. The animals (2 g dry weight) were soaked in methanol (50 mL) at -20 °C for 2 weeks, the methanol was evaporated, and the remaining aqueous suspension was washed with hexane (3 × 50 mL). The hexane extract was dried over sodium sulfate and the solvent evaporated to give a crude oil (30 mg, 1.5% dry weight) in which olepupuane (3) was clearly a major component. The oil was chromatographed by LC on Partisil with 1:1 ether/hexane as the eluant and then on Partisil ODS with 30% aqueous methanol as the eluant to give olepupuane (3; 2 mg, 0.1% dry weight).

Ninety-two specimens of *Dorioposilla albopunctata* (average length 10 mm) were collected in July 1981 at South Bird Rock, La Jolla, and Sunset Cliffs, San Diego. The animals (3.7 g dry weight) were soaked in methanol at -20 °C for 2 days, and the solvent was then extracted with dichloromethane (4 × 25 mL). The crude extract (1.21 mg, 3.2% dry weight) was chromatographed by LC on Partisil with 1:1 ether/hexane as the eluant to give the methoxy acetal 4 (4.5 mg, 0.1% dry weight).

Nine specimens of *D. albopunctata* (82-078) were collected by hand by using SCUBA (-6 m) in April 1982 at Bahia de los Angleles, Baja California, Mexico. The animals (2.7 g dry weight) were stored in acetone (~20 mL) at 0 °C for 3 weeks. The acetone extract was treated according to the procedure outlined for *D. krebsii* to yield olepupuane (3; 1 mg, 0.1 mg/animal) and a mixture of sesquiterpene esters 5 (1 mg, 0.1 mg/animal).

Two specimens (0.4 g dry weight) of *Doriopsilla janaina* (82-110) were collected at Bahia de los Angeles, Mexico, and were stored in acetone at -20 °C for 3 weeks. The acetone extract was treated according to the procedure outlined above and gave fats, sterols, olepupuane (3, 0.15 mg/animal), and the sesquiterpene esters 5 (0.15 mg/animal).

One hundred and ten specimens (32.5 g dry weight) of an undescribed yellow porostome nudibranch (82-073) were collected at Bahia de los Angeles, Baja California, in April 1982 and stored in acetone (700 mL) for 1 week. The extract was treated according to the procedure outlined above and gave olepupuane (3, 0.15 mg/animal) and a mixture of sesquiterpene esters 5 (0.4 mg/animal).

Forty-one specimens (26.7 g dry weight) of the giant brown porostome (82-072) were collected at Bahia de los Angeles, Mexico, and were stored in acetone at -20 °C for 3 weeks. The acetone extract was treated according to the standard procedures and gave fats, sterols, and the sesquiterpene esters 5 (2.7 mg/animal).

Fifteen specimens (0.9 g dry weight) of Fay's porostome (82-102) were collected intertidally at Bahia de los Angeles and were stored in acetone at -20 °C for 1 week. The acetone extract was treated according to the standard procedures and gave fats, sterols, and the sesquiterpene esters 5 (2.8 mg/animal).

Polygodial (1): $[\alpha]^{30}_D$ -97° (*c* 0.35, $CHCl_3$) (lit.[7] $[\alpha]^{25}_D$ -131°); UV (MeOH) 230 nm (ε 7000); IR ($CHCl_3$) 2923, 1720, 1677, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.54 (d, 1 H, *J* = 4.4 Hz), 9.46 (s, 1 H), 7.13 (m, 1 H), 2.84 (m, 1 H), 2.55–2.30 (m, 2 H), 1.95–1.15 (m, 7 H), 0.95 (s, 3 H), 0.93 (s, 3 H), 0.90 (s, 3 H); mass spectrum, *m/z* (relative intensity) 234 (M^+, 5), 206 (M^+ – CO, 100), 191 (M^+ – CO – CH_3, 73), 121 ($C_9H_{13}^+$, 61), 109 ($C_8H_{15}^+$, 52); HRMS, *m/z* 206.1675 ($C_{14}H_{22}O$ requires 206.1671).

Olepupuane (3): $[\alpha]_D$ -83.3° (*c* 0.54, $CHCl_3$), -51° (*c* 1.29, hexane); IR (CH_2Cl_2) 3024, 2992, 1732, 1423, 1262 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.53 (2 overlapping d, 2 H, *J* = 2.3, 1.8 Hz), 5.65 (m, 1 H), 2.58 (m, 1 H), 2.07 (s, 3 H), 2.04 (s, 3 H), 1.9–0.9 (m, 9 H), 0.84 (s, 3 H), 0.80 (s, 3 H), 0.78 (s, 3 H); ^1H NMR (CCl_4) δ 6.29 (m, 2 H), 5.59 (m, 1 H), 2.46 (m, 1 H), 2.05 (s, 3 H), 2.01 (s, 3 H), 0.87 (s, 3 H), 0.83 (s, 3 H), 0.80 (s, 3 H); ^1H NMR (C_6D_6) δ 6.70 (d, 1 H, *J* = 2.3 Hz), 6.13 (d, 1 H, *J* = 1.8 Hz), 1.56 (s, 3 H), 0.76 (s, 3 H), 0.61 (s, 3 H), 0.54 (s, 3 H); ^{13}C NMR (C_6D_6) δ 170.0, 168.8, 140.3, 124.1, 98.7, 65.8, 61.2, 47.8, 42.4, 39.5, 37.2, 33.5, 33.2, 28.9, 21.7, 21.1, 20.8, 19.0, 13.6; mass spectrum, *m/z* 336 (M^+, 2), 276 (M^+ – AcOH, 53), 234 (M^+ – AcOH – CH_2CO, 100); HRMS, *m/z* 276.1702 ($C_{17}H_{24}O_3$ requires 276.1725).

Methoxy acetal 4: $[\alpha]_D$ -17.2° (*c* 0.25, $CHCl_3$); IR (neat) 1745 cm^{-1}; ^1H NMR (CCl_4) δ 6.15 (d, 1 H, *J* = 4 Hz), 5.69 (m, 1 H, *J* = 3, 3, 3 Hz), 4.96 (s, 1 H), 3.26 (s, 3 H), 2.48 (m, 1 H, *J* = 4, 3, 3 Hz), 2.20 (m, 1 H, *J* = 18, 5, 3 Hz), 2.01 (s, 3 H), 1.92 (m, 1 H, *J* = 18, 12, 3, 3 Hz), 1.35 (dd, 1 H, *J* = 12, 5 Hz), 0.91 (s, 3 H), 0.89 (s, 3 H), 0.80 (s, 3 H); mass spectrum, *m/z* 308 (M^+), 248 (M^+ – AcOH); HRMS, *m/z* 248.1775 ($C_{16}H_{24}O_2$ requires 248.1776).

Sesquiterpene esters 5: IR ($CHCl_3$) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.31 (d, 1 H, *J* = 2 Hz), 6.04 (m, 1 H, $w_{1/2}$ = 4 Hz), 5.36 (m), 2.81 (m), 2.49 (m, 1 H, *J* = 12, 4, 2 Hz), 2.30 (m, 1 H, *J* = 12, 12, 2 Hz), 2.28 (m, 1 H), 1.26 (br s), 0.88 (s, 3 H), 0.82 (s, 3 H), 0.81 (s, 3 H) (signals with unspecified numbers of protons are due to protons in the fatty acid chains).

The fatty acid portions of the sesquiterpene esters 5 were analyzed as follows: a sample of the sesquiterpene esters 5 in 1:1 methanol/dichloromethane was added to ice-cold 10% sulfuric acid in methanol, and the solution was stirred at 0 °C for 1 h. The reaction mixture was partitioned between ether and aqueous sodium bicarbonate solution. The ether phase was dried over sodium sulfate and the solvent evaporated to yield euryfuran (8), identical in all respects with an authentic sample, and a mixture of carboxylic acid methyl esters. The methyl esters were analyzed by GC on a 6-ft column of Silar 5CP by using a Varian 3700 instrument (T_1, 185 °C, 10 min; 5 °C/min for 9 min; T_2, 230 °C, 11 min). *D. albopunctata*: n-15:0, 7%; n-16:0, 2%; n-18:0, 9%; n-18:1, 3%, n-18:2, 18%; n-18:3, 9%; n-20:1, 7%. *D. janaina*: n-14:0, 10%; n-15:0, 2%; n-16:0, 18%, n-17:0, 1%; n-18:0, 19%; n-18:1, 6%; n-18:2, 1%; n-20:0, 1%;, n-20:1, 9%; n-20:3, 6%; n-20:4, 12%; n-20:5, 6%. "Gulf yellow porostome": n-14:0, 1%; n-15:0, 10%; n-16:0, 5%; n-16:1, 3%; n-17:0, 3%; n-18:0, 4%; n-18:1, 13%; n-18:2, 2%; n-18:3, 4%; n-20:0, 1%; n-20:1, 3%; n-20:4, 4%; n-20:5, 3%. "Giant brown porostome": n-14:0, 2%; n-15:0, 5%; n-16:0, 16%; n-17:0, 85: n-20:1, 5%; n-20:3, 50%. "Fay's porostome": n-15.0, ~10%; n-16:0, ~30%, n-16:1, ~40%.

Acid Treatmnt of Olepupuane (3). A portion of olepupuane (3, 1.0 mg) was dissolved in 1.0 mL of CH_2Cl_2. A small crystal of *p*-toluenesulfonic acid (*p*-TsOH) was added, and the solution was stirred at room temperature for 1 h. TLC of the reaction mixture (silica gel; hexanes/EtOAc, 7:3) revealed that no starting material remained and that a single UV-absorbing spot with an R_f corresponding to that of polygodial appeared. HLPC (μ-Lichrosorb Si-60, 70:30 hexanes/EtOAc) of the reaction mixture afforded 0.6 mg of one dialdehyde, which was shown by MS, ^1H

NMR, and UV analysis to be polygodial (1).

Reduction of Olepupuane (3) with Lithium Aluminum Hydride. Lithium aluminum hydride (10 mg) was added to a solution of olepupuane (3; 0.5 mg, 0.002 mmol) in dry THF (5 mL), and the reaction mixture was stirred at 0 °C for 35 min. excess reagent was destroyed with ethyl acetate, and the reaction products were partitioned between dichloromethane (4 × 5 mL) and 5% aqueous hydrochloric acid (10 mL). The combined dichloromethane extracts were dried over sodium sulfate, and the solvent was evaporated to yield a crude product that was purified by LC on Partisil with ethyl acetate as the eluant to yield the diol 6: 0.3 mg (85% theoretical); IR (neat) 3340 cm^{-1}; ^1H NMR (CCl_4) δ 5.70 (m, 1 H, J = 3, 3, 1 Hz), 4.20 (dd, 1 H, J = 12, 1 Hz), 3.87 (d, 1 H, J = 12 Hz), 3.78 (dd, 1 H, J = 11, 2 Hz), 3.57 (dd, 1 H, J = 11, 8 Hz), 0.88 (s, 6 Hz), 0.75 (s, 3 H); mass spectrum, m/z (relative intensity) 238 (M^+, 10), 220 (5), 207 (8), 191 (90), 190 (100).

Reduction of Methoxy Acetal 4 with Lithium Aluminum Hydride. By use of the method described above, a solution of methoxy acetal 4 (1 mg, 0.003 mmol) in tetrahydrofuran (5 mL) was reduced with lithium aluminum hydride (10 mg) at 0 °C to yield the diol 6 (0.7 mg, 91% theoretical), having spectral data identical with those of the authentic material.[12]

Acknowledgment. We thank Scott Johnson (Hawaii) and James R. Lance (La Jolla) for identification of the nudibranchs. P.J.S. thanks Dr. Gary Schulte for collection, Drs. Schulte and Robin Kinnel for helpful discussions, Lars Bergknut and Karl Yanagihara for mass spectral determinations, and the Southern California Regional NMR Facility (W. Croasmun, Director) for an NOE experiment. This research was supported by grants from the National Science Foundation (to P.J.S. and D.J.F.) and from the University of Hawaii Sea Grant College Program.

Registry No. 1, 6754-20-7; 3, 85356-02-1; 4, 85356-03-2; 6, 34437-62-2; 8, 79895-94-6.

Occurrence of Longicaudatine, a New Type of Bis-Indole Base and Bisnor-C-alkaloid H in *Strychnos* Species

G. Massiot, M. Zeches, C. Mirand, and L. Le Men-Olivier

Faculté de Pharmacie, ERA 319 CNRS, 51096 Reims Cedex, France

C. Delaude

Université de Liège, Sart Tilman, Liège, Belgium

K. H. C. Başer,* R. Bavovada, N. G. Bisset, and P. J. Hylands

Pharmacognosy Research Laboratories, Department of Pharmacy, Chelsea College, University of London, London SW3 6LX, England

J. Strömbom

Department of Pharmacognosy, Faculty of Pharmacy, Biomedicum, S-751 23 Uppsala, Sweden

R. Verpoorte

Department of Pharmacognosy, Subfaculty of Pharmacy, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands

Received July 16, 1982

The structure of longicaudatine, a novel bis-indole alkaloid isolated from several *Strychnos* species, has been elucidated chiefly by 400-MHz ^1H NMR and ^{13}C NMR spectroscopy. In some species this alkaloid co-occurs with bisnor-C-alkaloid H, an isomeric base which has similar chromatographic and chromogenic properties.

During the screening of Asian *Strychnos* material, tertiary alkaloid extracts from the root bark of *S. axillaris* Colebr., *S. ignatii* Berg., and *S. nux-vomica* L. were observed to include several minor components which on thin-layer chromatograms immediately colored blue when sprayed with iron(III) chloride–perchloric acid reagent.[1] One of these blue-coloring bases was later isolated from the root bark of *S. nux-vomica*,[2] but the minute amount obtained at the time precluded any attempt to determine the structure. A further quantity of the compound has now been obtained from the root bark of *S. lucida* R.Br.,[3] and it is also present in *S. wallichiana* Steud. ex DC.[4] The substance appears to be identical with an alkaloid occurring in greater amount in the stem bark of the African species *S. dolichothyrsa* Gilg ex Onochie et Hepper[5] and also detected in *S. urceolata* Leeuwenberg,[6] *S. afzelii* Gilg,[7] and *S. chrysophylla* Gilg.[4]

The various products have proved to be closely related to, if not identical with, each other. Initially, the spec-

* Present address: Faculty of Pharmacy, University of Anatolia, Eskişehir, Turkey.

(1) (a) Bisset, N. G.; Phillipson, J. D. *Lloydia* **1976**, *39*, 263. (b) Bisset, N. G.; Başer, K. H. C.; Phillipson, J. D.; Bohlin, L.; Sandberg, F. *Ibid.* **1977**, *40*, 546.
(2) Başer, K. H. C. Ph. D. Thesis, University of London, 1978, pp 82, 186.
(3) Bavovada, R., 1980, unpublished results.
(4) Strömbom, J., 1981, unpublished results.
(5) (a) Verpoorte, R. Ph.D. Thesis, University of Leiden, 1976, p 115. (b) Verpoorte, R.; Verzijl, M. J.; Baerheim Svendsen, A. *Planta Med.* **1982**, *34*, 21.
(6) Verpoorte, R.; Kodde, E. W.; Baerheim Svendsen, A. *Planta Med.* **1978**, *34*, 62.
(7) Verpoorte, R.; Kodde, E. W.; van Doorne, H.; Baerheim Svendsen, A. *Planta Med.* **1978**, *33*, 237.

0022-3263/83/1948-1869$01.50/0