27.1 *t*, 125.5 *d*, 141.1 *s*, 35.4 *t*, 26.7 *t*, 34.5 *d*, 135.2 *s*, 122.5 *t*, 167.2 *s*, 15.8 *q*, 66.2 *t*, 61.4 *t*, 19.6 *q*; OMe: 51.1 *q*; OAc: 20.3 *q*, 170.3 *s* (a few triplets may be interchangeable).

Acknowledgement—We thank the Deutsche Forschungsgemeinschaft for financial support.

REFERENCES

1. Robinson, H. and King, R. M. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L. eds) p. 465. Academic Press, London.
2. Jakupovic, J., Pathak, V. P., Bohlmann, F., Gage, D. and Dillon, M. O. (1986) *Phytochemistry* **25**, 2563.
3. Bohlmann, F. and Zdero, C. (1971) *Chem. Ber.* **104**, 964.
4. Dolejs, L. and Herout, V. (1962) *Coll. Czech. Chem. Comm.* **27**, 2654.
5. Doskotsch, R. W. and El-Feraly, F. S. (1970) *J. Org. Chem.* **35**, 1928.
6. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1985) *Planta Med.* 76.
7. Bohlmann, F., Schmeda-Hirschmann, G. and Jakupovic, J. (1984) *Phytochemistry* **23**, 1435.
8. Drozdz, B., Grabarczyk, H., Samek, Z., Holoub, M., Herout, V. and Sorm, F. (1972) *Coll. Czech. Chem. Comm.* **37**, 1546.
9. Herz, W. and Kumar, N. (1981) *Phytochemistry* **20**, 1339.
10. Bohlmann, F., Zdero, C. and Turner, B. L. (1984) *Phytochemistry* **23**, 1055.
11. Romo, J., Rios, T. and Quijano, L. (1968) *Tetrahedron* **24**, 6087.
12. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1986) *Lieb. Ann. Chem.* 799.
13. Bohlmann, F., Dutta, L. N., Dorner, W., King, R. M. and Robinson, H. (1979) *Phytochemistry* **18**, 673.
14. Warning, U., Friedrich, D., Castro, V. and Bohlmann, F. (1987) *Phytochemistry* **26**, 2331.
15. Bohlmann, F., Mahanta, P., Suwita, A., Suwita, Ant., Natu, A. A., Zdero, C., Dorner, W., Ehlers, D. and Grenz, M. (1977) *Phytochemistry* **16**, 1973.
16. Boeker, R., Jakupovic, J., Bohlmann, F., King, R. M. and Robinson, H. (1986) *Phytochemistry* **25**, 1669.
17. Bohlmann, F., Ates (Gören), N., Jakupovic, J., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1180.
18. Bohlmann, F. and Zdero, C. (1981) *Phytochemistry* **21**, 2431.
19. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1979.

Phytochemistry, Vol. 27, No. 2, pp. 621–623, 1988.
Printed in Great Britain.

0031–9422/88 $3.00+0.00

SPHAEROPYRANE, A DITERPENE FROM THE MARINE RED ALGA *SPHAEROCOCCUS CORONOPIFOLIUS*

Francesco Cafieri, Lorenzo de Napoli, Ernesto Fattorusso and Ciro Santacroce*

Dipartimento di Chimica delle Sostanze Naturali, Università di Napoli, Via L. Rodinò 22, 80138 Naples, Italy;* Dipartimento di Chimica Organica e Biologica, Università di Napoli, Via Mezzocannone 16, 80134 Naples, Italy

(*Revised received* 17 *June* 1987)

Key Word Index—*Sphaerococcus coronopifolius*; Rhodophyta; diterpenes; sphaeropyrane.

Abstract—A new diterpene, sphaeropyrane has been isolated from the marine red alga *Sphaerococcus coronopifolius*. Its structure has been assigned mainly on the basis of ^{1}H and ^{13}C NMR experiments.

INTRODUCTION

The cosmopolitan bright-red alga *Sphaerococcus coronopifolius*, generally growing on rocks in shallow places, has been the subject of numerous studies for secondary metabolites [1–13]. Until now 18 new diterpenes based on six new rearranged polycyclic skeletons have been isolated and their biogenesis has been hypothesized [9, 10, 11]. This paper reports on the isolation of sphaeropyrane (**1**), a compound which belongs to a new class of diterpenes with a non-rearranged carbon skeleton.

Stereostructure **1** (relative stereochemistry) has been based on spectral data including extensive spin decoupling experiments and 2D ^{13}C–^{1}H shift correlated NMR spectroscopy via ^1J, ^2J and ^3J.

RESULTS AND DISCUSSION

A chloroform extract of the freeze-dried *S. coronopifolius*, after repeated chromatographies over silica gel, provided crude **1** which was purified by reversed-phase HPLC to yield **1** (0.003% dry weight), $C_{20}H_{32}O$ (HRMS), mp 136–138°.

Sphaeropyrane was recognized to possess a $-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-$ group by IR (ν_{max} 1025, 1070 and 1120 cm^{-1}) and by

^{13}C NMR spectroscopy, which showed signals at δ72.94 and 84.01 due to two non-protonated carbon atoms as deduced from DEPT (Distortless Enhancement by Polarization Transfer). Further NMR signals showed the presence of three methyls (^{13}C NMR DEPT: δ30.18, 34.63, 19.98; ^{1}H NMR: 3H singlets, at δ1.31, 1.52 and 0.91) and a vinyl group (^{13}C NMR DEPT: δ145.76 (CH) and 110.79 (CH_2); ^{1}H NMR: double-doublets at δ5.67, 5.33 and 4.96) all of them linked to non-protonated carbon atoms.

An accurate analysis of the 500 MHz ^{1}H NMR spectrum, assisted by decoupling and decoupling-difference experiments, defined the constellations C-15–16–17–18–19–20, C-6–7–8 and C-2–3–4 (Table 1).

These attributions were confirmed by ^{1}H–^{13}C correlation via ^{1}J, which allowed the assignments of all the protonated carbon atoms (Table 1). Evidence that furnished a basis for a logical way in which to combine the above part structures was provided by heteronuclear ^{1}H–^{13}C 2D NMR spectroscopy correlation via ^{2}J and ^{3}J. This experiment led to the unambiguous positioning of the carbon atoms C-1 (which correlates with H-10 and H_b-14), C-5 (which correlates with H-12), C-9 (which correlates with H-11) and C-18 (which correlates with H-19 and H-20).

The relative stereochemical features of **1** were resolved by the NOED measurements depicted Fig. 1. Irradiation of the H_2-7 signal at δ0.46 resulted in the enhancement of both H_a-14 (δ5.33) and H_{ax}-3 (δ0.98) resonances. This experiment was fortuitous in that it successfully related the relative stereochemistries of five carbon atoms (C-1, C-4, C-6, C-8 and C-9) belonging to the three rings of **1**. The enhancement of the signal at δ0.98 can only occur if the pyrane and cyclopentane rings are *cis*-fused and if H_2-7 is *trans* to H-4 and H_3-11. Moreover, the enhancement of the signal at δ5.33 not only confirms the above stereochemical features but also requires that the cyclopropane ring and the vinyl group at C-12 are both on the same face of the molecule as shown in Fig. 1.

Finally the relative stereochemistry at C-5 was deduced from the nOe enhancement of H-4 observed on irradiation of the H_3-12 frequency which established their *cis*-relationship.

Sphaeropyrane possesses an unprecedent tricyclic skeleton and represents the first diterpenoid with a biogenetically regular ring system isolated from *S. coronopifolius*. Its biogenesis could be logically formulated from geranylgeraniol *via* the intermediacy of geranyllinalol by loss of a H^- followed by intramolecular cyclization as shown in Scheme 1.

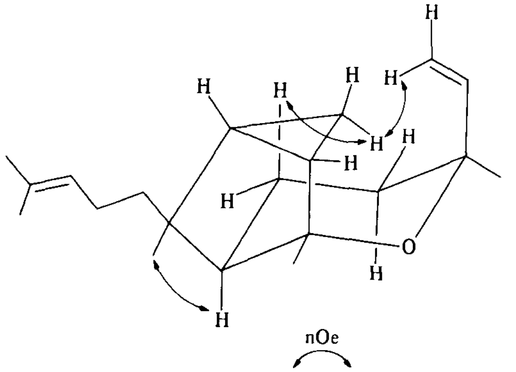
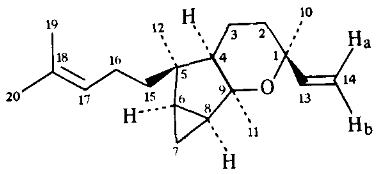


Figure 1.



Formula 1.

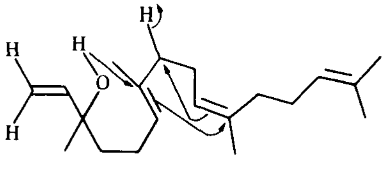
EXPERIMENTAL

General. Optical rotation: $CHCl_3$ (*c* 0.8). ^{1}H NMR: 500.13 MHz ($CDCl_3$ soln, TMS as internal standard). ^{13}C NMR spectra, NOED and 2D NMR: 250.13 and 62.96 MHz for ^{1}H and ^{13}C respectively using a ^{1}H–^{13}C dual probe. One bond and long range ^{1}H–^{13}C shift correlated 2D NMR spectra were carried out with a Bruker microprogram adjusting fixed delays to give maximum polarization for $J_{C-H} = 135$ and 7.25 Hz respectively. Two DEPT experiments at 250 and 62.96 MHz were performed using polarization transfer pulses at 90° and 135°, respectively, obtaining in the first case only signals for CH group and in the other case positive signals for CH and Me and negative ones for CH_2 groups.

Plant material. The alga (*S. coronopifolius*) was collected in the bay of Naples during Spring 1986. A voucher specimen is deposited at the Dipartimento di Chimica Organica e Biologica, Naples, Italy.

Isolation of sphaeropyrane (**1**). Fresh material (1250 g, dry after extraction) was freeze-dried, ground with a blender and extracted × 4 with $CHCl_3$ at room temp. for 2 days. Combined extracts were taken to dryness under red. pres. and the oily residue (5.7 g) was chromatographed on a silica gel. (570 g) column using eluent of increasing polarity form hexane to Et_2O. Selected fractions eluted with hexane–Et_2O (7:3), taken to dryness, afforded 320 mg of an oily product which was rechromatographed on a silica gel column (30 g) using as eluent hexane-$CHCl_3$ (8:2), thus obtaining 53 mg of crude **1**, which was purified by reversed phase HPLC using a RP-18 (1 × 25 cm, Merck) column (eluent CH_3CN) to give pure **1**, 37 mg, mp 136–138°; $[\alpha]_D -43.9°$; high-resolution EIMS, observed *m/z* 288.2454, $C_{20}H_{32}O$ requires 288.2453.

Acknowledgements—This study was supported by the Italian MPI and C. N. R. (Progetto Finalizzato 'Chimica Fine e Secondaria'). We acknowledge the skilful technical assistance of Miss Rita Carolla.



Scheme 1.

Table 1. NMR spectral data for sphaeropyrane (1)

Position	^{1}H (Multiplicity)*	^{13}C†	^{13}C–^{1}H long-range correlations
1		72.94	C1-H10, C1-Hb14
2	1.70 (H_{eq}, *ddd*, $J_{2eq-2ax} = 13$) $J_{2eq-3eq} = 5$) $J_{2eq-3ax} = 2$) 1.25 (H_{ax}, *ddd*, $J_{2ax-3ax} = 13$)	34.91	
3	1.23 (H_{eq}, *ddd*, $J_{3eq-3ax} = 13$) $J_{3eq-4} = 5$) 0.98 (H_{ax}, *ddd*, $J_{3ax-4} = 13$)	21.52	
4	1.44 (H, *dd*,)	55.20	
5		45.32	C5-H12
6	1.49 (H, *m*)	29.91	
7	0.46 (2H, complex signal)	7.68	
8	1.24 (H, *m*)	31.56	
9		84.01	C9-H11
10	1.31 (3H, *s*)	30.18	
11'	1.52 (3H, *s*)	34.62	
12	0.91 (3H, *s*)	19.98	
13	5.67 (H, *dd*, $J_{13-14a} = 15$) $J_{13-14b} = 10$)	145.76	
14a	5.33 (H, *dd*, $J_{14-14b} = 2$)	110.79	
14b	4.96 (H, *dd*)		
15	1.40 (2H, *m*)	46.03	
16	1.94 (2H, *m*)	23.43	
17	5.09 (1H, *br t*, $J_{17-16} = 7.5$)	124.88	
18		131.19	C18-H19, C18-H20
19	1.67 (3H, *br s*)	25.66	
20	1.60 (3H, *br s*)	17.57	

*Coupling constants J are in Hz.

†Assignments based on ^{13}C–^{1}H shift correlated 2D NMR spectroscopy via ^1J couplings, which showed the interrelation of all protonated carbons with the pertinent proton(s). The non-protonated carbon atoms were assigned on the bases of long-range ^{13}C–^{1}H shift correlated 2D NMR spectroscopy. The number of proton(s) attached to carbons was determined by DEPT experiments.

REFERENCES

1. Fenical, W., Finer, J. and Clardy, J. (1976) *Tetrahedron Letters* 731.
2. Fattorusso, E., Magno, S., Santacroce, C., Sica, D., Di Blasio, B., Pedone, C., Impellizzeri, G., Mangiafico, S., Oriente, G., Piattelli, M. and Sciuto, S. (1976) *Gazz. Chim. It.* **106**, 779.
3. Cafieri, F., De Napoli, L., Fattorusso, E., Impellizzeri, G., Piattelli, M. and Sciuto, S. (1977) *Experientia* **33**, 1549.
4. Cafieri, F., De Napoli, L., Fattorusso, E., Piattelli, M. and Sciuto, S. (1979) *Tetrahedron Letters* 963.
5. Cafieri, F., Fattorusso, E., Di Blasio, B. and Pedone, C. (1981) *Tetrahedron Letters* **22**, 4123.
6. Cafieri, F., Ciminiello, P., Fattorusso, E. and Santacroce, C. (1982) *Experientia* **38**, 298.
7. Cafieri, F., Ciminiello, P., Santacroce, C. and Fattorusso, E. (1982) *Phytochemistry* **21**, 2412.
8. Cafieri, F., Ciminiello, P., Santacroce, C. and Fattorusso, E. (1983) *Phytochemistry* **22**, 1824.
9. Cafieri, F., Fattorusso, E. and Santacroce, C. (1984) *Tetrahedron Letters* **25**, 3141.
10. Cafieri, F., Fattorusso, E., Mayol, L. and Santacroce, C. (1985) *J. Org. Chem.* **50**, 3982.
11. Cafieri, F., Fattorusso, E., Mayol, L. and Santacroce, C. (1986) *Tetrahedron* **42**, 4273.
12. Bavoso, A., Cafieri, F., De Napoli, L., Di Blasio, B., Fattorusso, E., Santacroce, E. and Pavone, B. (1987) *Gazz. Chim. Ital.* (in press).
13. Cafieri, F., De Napoli, L., Fattorusso, E. and Santacroce, C. (1987) *Phytochemistry* **26**, 471.