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Note

X-ray structure of floridoside isolated from the marine red algae *Dilsea carnosa*

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ABSTRACT

The natural floridoside (2-*O*-α-D-galactopyranosylglycerol) was isolated from *Dilsea carnosa*, and its structure has been determined by single-crystal X-ray diffraction analysis. The solved structure is in agreement with the previously solved crystal structure of floridoside [Simon-Colin, C.; Michaud, F.; Léger, J.-M.; Deslandes E. *Carbohydr. Res.* **2003**, *338*, 2413–2416] and demonstrates for the first time the presence of floridoside in the red algae *Dilsea carnosa*.

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Floridoside is the main photosynthetic and reserve product in all orders of the Rhodophyta except the Ceramiales,[1,2] and it is believed to also act as an osmotic regulator.[3,4]

Evidence of its occurrence in several red algae has been described,[5–7] and recently a single-crystal X-ray diffraction analysis was performed for floridoside crystals obtained from *Palmaria palmata*.[5] Here, we describe the first direct evidence for the occurrence of floridoside in the red algae *Dilsea carnosa* (Schnidel) Kuntze (Gigartinales, *Dumontiaceae*) through a new crystal X-ray diffraction analysis of natural floridoside isolated from this Rhodophyta. The results reported herein are direct evidence for the structure and absolute configuration of natural floridoside, confirming that obtained from *P. palmata*.

The crystal obtained from *D. carnosa* was submitted to X-ray diffraction analysis, which permitted us to assign the structure of the compound without any doubt (see Fig. 1). The crystal was orthorhombic, with a space group $P2_12_12_1$ (see Table 1). Research based on the solved structure showed that it corresponds to floridoside, whose crystal structure has been previously solved.[5] Our cell parameters, as well as the floridoside conformation in the crystal, are the same as that published.[5] The six-membered ring takes a chair conformation in the crystal, and the absolute configuration of five carbons in the cycle is: C3 (*R*), C5 (*S*), C6 (*R*), C8 (*S*), C10 (*R*).

The crystal packing of floridoside is ensured through a complex network of hydrogen bonds occurring between neighboring molecules. All six hydroxyl groups are engaged in the H-bonds with neighboring hydroxyl groups (see Fig. 2, Table 2). It is interesting to note that each hydroxyl group participates at the same time in the formation of two hydrogen bonds, that is, OH is at the same time both a donor of a hydrogen bond and an acceptor of a hydrogen bond (Fig. 2, Table 2).

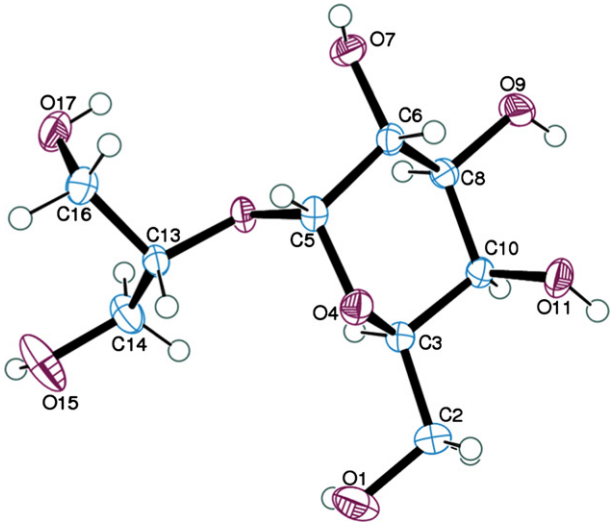

Figure 1. View of floridoside showing the labeling of the non-hydrogen atoms. Thermal ellipsoids are shown at the 50% probability levels; hydrogen atoms are drawn as small circles of arbitrary radius.

1. Experimental

1.1. Material

D. carnosa was collected from the French channel coast at Langrunes in Normandy, France. A total of 500 g of fresh material

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Table 1
Crystal data and structure refinement for floridoside

Empirical formula	$C_9H_{18}O_8$
Formula weight	254.23 g/mol
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	$a = 4.88440(10)$ Å, $\alpha = 90°$ $b = 9.7259(3)$ Å, $\beta = 90°$ $c = 23.8754(6)$ Å, $\gamma = 90°$
Volume	1134.21(5) Å^3
Z, Calculated density	4, 1.489 Mg/m^3
Absorption coefficient	0.132 mm^{-1}
F(000)	544
Crystal size	0.649 × 0.431 × 0.351 mm
Theta range for data collection	2.70 to 38.67°
Limiting indices	$-8 \leqslant h \leqslant 8$, $-16 \leqslant k \leqslant 16$, $-41 \leqslant l \leqslant 41$
Reflections collected/unique	63701/6386 [R(int) = 0.0264]
Completeness to theta = 38.67	99.8%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6386/0/226
Goodness-of-fit on F^2	1.095
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0326$, $wR_2 = 0.0852$
R indices (all data)	$R_1 = 0.0392$, $wR_2 = 0.0894$
Absolute structure parameter	0.1(4)
Largest diff. peak and hole	0.362 and −0.210 e Å^{-3}

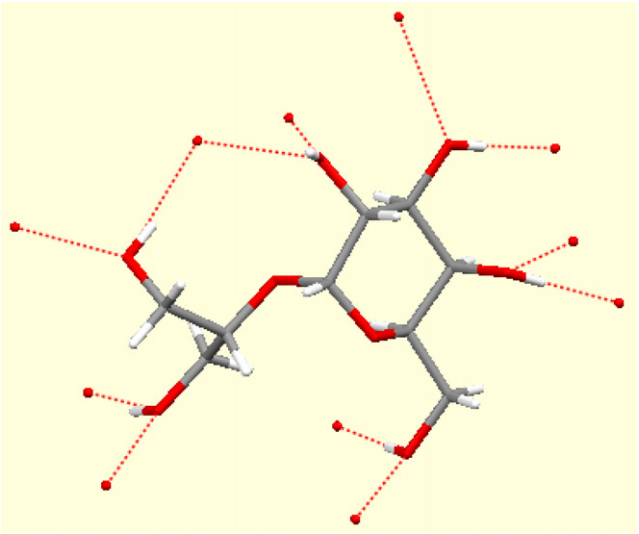

Figure 2. A view of hydrogen bonds in the crystal packing of floridoside. Dashed lines indicate the H-bonds.

was subsequently washed twice with sea water, then briefly with water before freezing at −20 °C.

1.2. Floridoside isolation

Lyophylized powdered plant material (105 g) was extracted three times with 60% EtOH (10% w/v), during 24 h under magnetic stirring, at room temperature. The aqueous alcoholic extract was concentrated to dryness to obtain 10 g of a solid residue. The residue (10 g) was redissolved in water and successively extracted with cyclohexane, CH_2Cl_2, EtOAc, and BuOH for further studies. The resultant aqueous residue was concentrated to dryness, and 200 mg of the 5 g obtained was subjected to column chromatography over LH-20 Sephadex (Sigma) and eluted with MeOH. Twelve fractions of 15 mL each were collected and monitored by TLC analysis. White floridoside crystals (5 mg, 3%) were obtained in fraction 5 after total evaporation of the MeOH under an extractor hood; mp 128.5 °C, lit.[5] 129 °C, lit.[6] 128.5 °C.

Table 2
Hydrogen bonds for floridoside [Å and °]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(7)–H(7)···O(11)$^{\#1}$	0.807(18)	1.896(18)	2.6887(8)	167.3(18)
O(11)–H(11)···O(17)$^{\#2}$	0.817(15)	1.795(15)	2.6105(9)	176.5(15)
O(9)–H(9)···O(7)$^{\#3}$	0.818(14)	1.930(14)	2.7466(8)	175.9(14)
O(1)–H(1)···O(1)$^{\#4}$	0.794(17)	1.951(16)	2.7444(7)	176.0(17)
O(17)–H(17)···O(9)$^{\#5}$	0.787(16)	1.914(16)	2.6906(9)	168.8(16)
O(15)–H(15)···O(15)$^{\#6}$	0.89(2)	1.91(2)	2.7808(7)	168(2)

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$: $-x+1, y-1/2, -z+3/2$; $^{\#2}$: $x, y+1, z$; $^{\#3}$: $-x+2, y+1/2, -z+3/2$; $^{\#4}$: $x+1/2, -y+1/2, -z+2$; $^{\#5}$: $-x+2, y-1/2, -z+3/2$; $^{\#6}$: $x+1/2, -y-1/2, -z+2$.

1.3. X-ray studies

Suitable crystals of the title compound were grown at 15 °C under an extractor hood, and they were mounted on glass fibers.

Diffraction data were collected at 150 K on a Bruker–Nonius Kappa II diffractometer equipped with a CCD area detector with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Data were measured using phi and omega scans. The data treatment was carried out with the APEX II program.[8] The crystal structure was solved by direct methods using the SHELXTL package[9] and refined using SHELX97.[10] All non-hydrogen atoms were refined anisotropically. All H atoms were determined via difference Fourier maps and refined with isotropic atomic displacement parameters. The temperature factors of fixed H-atoms were refined isotropically.

Supplementary data

Crystallographic data, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with CCDC No. 680442. Copies of the data can be obtained free of charge on application with the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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