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Note

Crystal structure and chirality of natural floridoside

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Abstract

The crystal structure and absolute configuration of natural floridoside (2-*O*-α-D-galactopyranosylglycerol) were determined by single-crystal X-ray diffraction analysis. The space group is orthorhombic $P2_12_12_1$ with $Z=4$, $a=4.885(1)$, $b=9.734(1)$, $c=23.886(2)$ Å at 296 ± 2 K. The structure was solved by a direct method and refined to $R=0.0351$ from 1914 reflections of Cu K_α radiation.

Keywords: Floridoside; X-ray crystal structure; Chirality

Floridoside (2-*O*-α-D-galactopyranosylglycerol) takes an important part in most of the red algae as a photosynthetic reserve product[1–4] and, very likely, as an intracellular osmotic regulator too.[5,6] Since its first isolation,[7] its molecular structure was determined by Putman and Hassid in 1954 by acetylation and per-methylation methods[8] and further refined by several NMR spectroscopy studies.[6,9–12] Recent improvements in its purification[12] made it possible to grow suitable crystals for a single-crystal X-ray diffraction analysis. The results are reported hereafter.

1. Experimental

Natural floridoside was extracted and purified as described elsewhere.[12] The melting point and rotatory power were found in good agreement with previous results: mp 129 °C, lit.[8] 128.5 °C, lit.[13] 127–127.5 °C, lit.[14] 132–134 °C; $[\alpha]_D$ +164° (*c* 0.97, water), lit.[8] $[\alpha]_D$ +165° (*c* 3.35, water), lit.[13] $[\alpha]_D$ +172° (*c* 0.7, water), lit.[14] $[\alpha]_D$ +162° (*c* 1, water). Crystals were grown at room temperature (rt) by diffusion of evaporated Et_2O in a concentrated ethanolic solution of floridoside. Intensities were collected at rt with an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Cu K_α radiation up to $\theta=65°$. The unit-cell dimensions were determined using least-squares fit from 25 reflections ($25<\theta<35°$). No intensity variation of two standard reflections monitored every 90 min was observed. The data were corrected for Lorentz and polarization effects and for absorption ("psi-scan" method).[15] The structure was solved by direct methods using SHELX 86 and refined using SHELX 97 suites of programs.[16,17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the last step of the refinement with isotropic thermal displacement parameters. A summary of the crystal data, data collection parameters and refinement results is given in Table 1. Atomic coordinates and displace-

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Table 1
Crystal data, data collection parameters and refinement results for floridoside

$C_9H_{18}O_8$	Colourless
$M = 254.24$	
Orthorhombic, $P2_12_12_1$	$Z = 4$
$a = 4.885(1)$ Å	$T = 296$ (2) K
$b = 9.734(1)$ Å	$\lambda = 1.5418$ Å (Cu K_α)
$c = 23.886(2)$ Å	$\mu = 0.115$ mm^{-1}
$V = 1135.8(3)$ Å^3	$D_x = 1.487$ Mg m^{-3}
1914 measured reflections	ω–2θ scans
1914 unique reflections	$4.91 < \theta < 64.75°$
1903 with $I > 2\sigma(I)$	$-5 \le h \le 5$
$F(000) = 544$	$0 \le k \le 11$
Max. Transmission 0.9998	$0 \le l \le 28$
Min. Transmission 0.9719	Completeness 99.7%
Full-matrix least-squares,	1914 data
Refinement on all F^2	161 parameters
For $I > 2\sigma(I)$ and all data, resp.,	$w = 1/[\sigma^2 + (0.0689P)^2 + 0.2502P]$
$R_1 = 0.035$ and 0.035	where $P = (F_o^2 + 2F_c^2)/3$
$wR_2 = 0.091$ and 0.092	Extinction coefficient 0.076(3)
$S = 1.031$	$\Delta\rho_{min} = 0.222$ e Å^{-3}
Flack coefficient $-0.03(19)$	$\Delta\rho_{min} = -0.198$ e Å^{-3}

ment parameters are available as supplementary materials.

The X-ray results confirm the structure as anticipated on the basis of ^{13}C and ^1H NMR data. An ORTEP view is shown in Fig. 1. All bond lengths and angles are consistent with an sp^3 valency:[18] C–C lengths range from 1.513(2) Å [C(11)–C(12) and C(12)–C(13)] to 1.529(2) Å [C(1)–C(2)] and C–O lengths, from 1.409(2) Å [C(1)–O(8)] to 1.442(2) Å [C(5)–O(7)]; angles are found between 106.55(14)° [O(8)–C(12)–C(13)] and 113.35(15)° [C(11)–C(12)–C(13)].

The absolute configuration of the molecule was reliably stated, according to the low value of the Flack coefficient.[19] The chirality of the asymmetric carbon atoms is: C(1) *S*, C(2) *R*, C(3) *S*, C(4) *R*, C(5) *R*. The molecule crystallises in chair conformation with the ramifications close to the mean plane. The conformation is stabilised by two weak intra-molecular hydrogen bonds: C(5)–H(5)···O(8) and C(12)–H(12)···O(7); angles C–H···O = 100.7 and 102.2°, distances H···O = 2.48 and 2.58 Å, respectively.

The molecular packing is shown in Fig. 2. Most of the contacts between molecules are of hydrogen-bond type. Each molecule is bound to its 10 neighbours by one or two such contacts, that gives rise to a three-dimensional network of hydrogen bonds.

2. Supplementary materials

Crystallographic data for this paper have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/conts/retrieving.html).

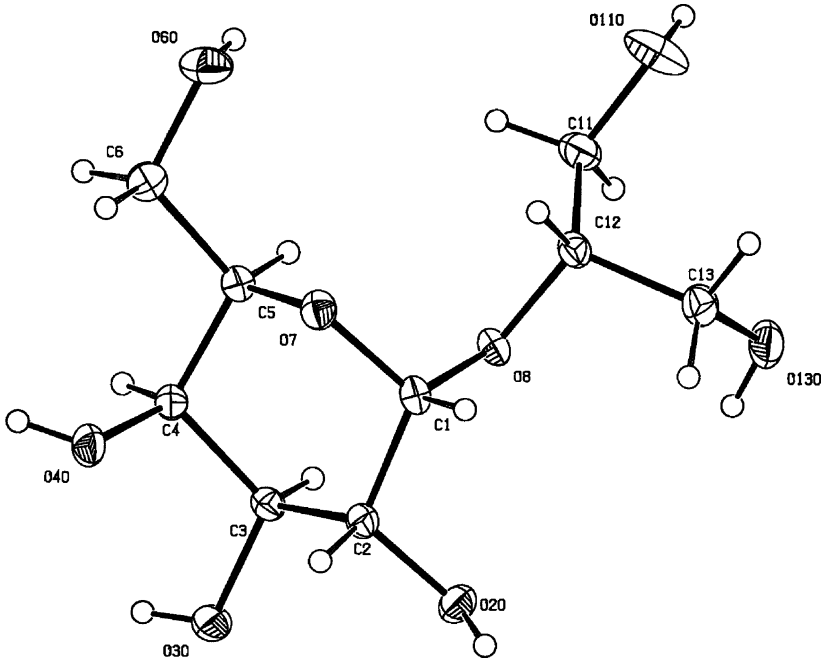

Fig. 1. ORTEP drawing of the molecule showing atom numbering. Displacement ellipsoids are drawn at the 50% probability level.

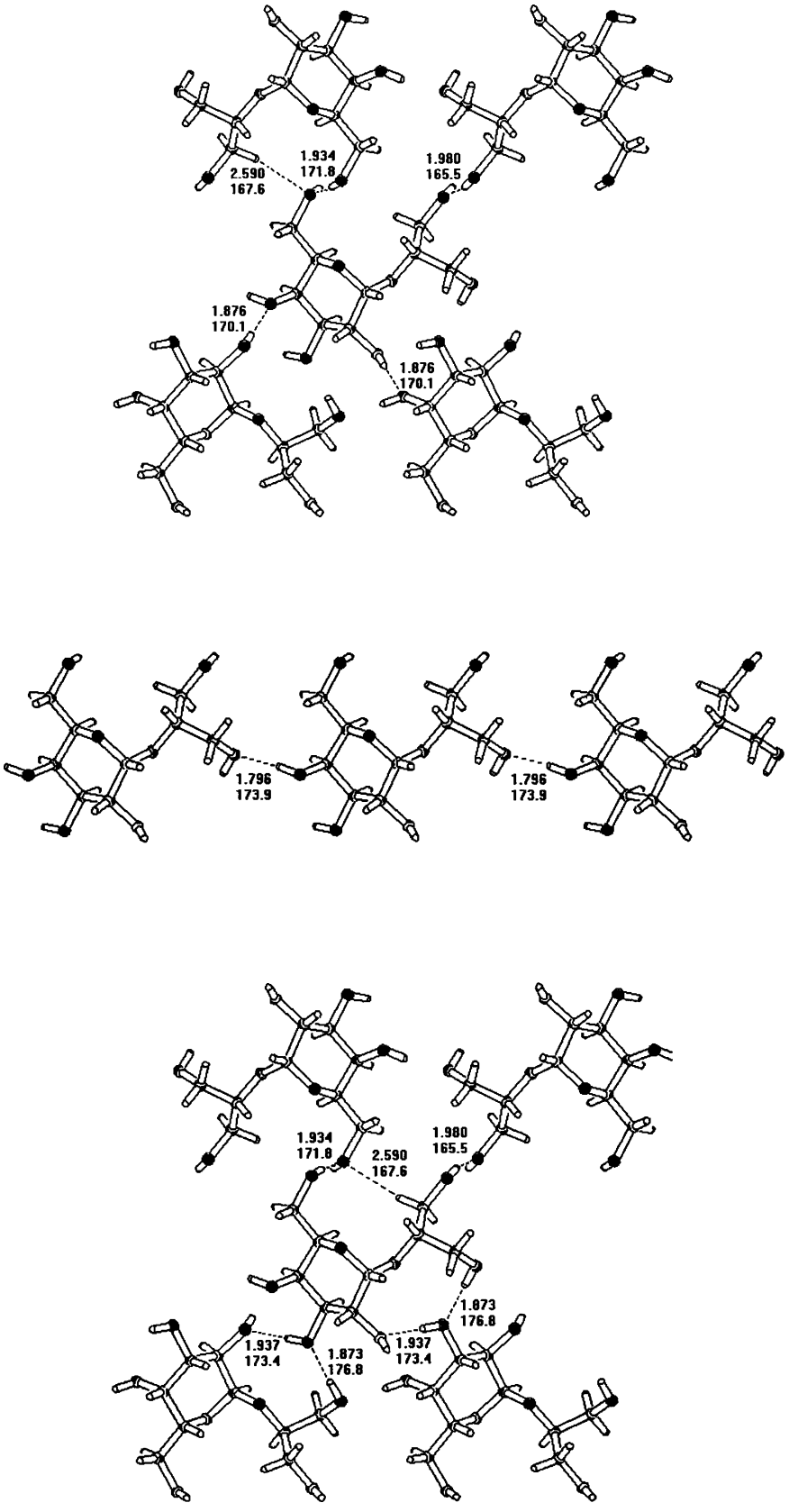

Fig. 2. Molecular packing with the inter-molecular hydrogen bonds (dashed lines) viewed along the axis. The three drawings display the connections of one molecule with its neighbours in higher (top), same (middle) and lower layer (bottom), respectively. Distances H···A and angles D–H···A are given in Å and °.

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