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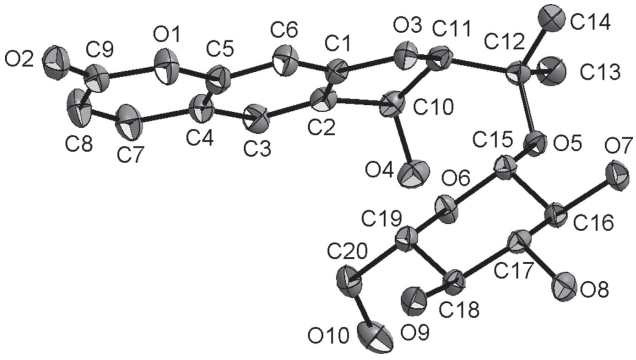
Crystal structure of 2-((2-(3-hydroxy-7-methylene-2,3-dihydro-7*H*-furo[3,2-*g*]chromen-2-yl)propan-2-yl)oxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol – a marmesin derivative, $C_{20}H_{24}O_{10}$



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Abstract

$C_{20}H_{24}O_{10}$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 6.3728(6)$ Å, $b = 14.3835(14)$ Å, $c = 20.453(2)$ Å, $V = 1874.8(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0272$, $wR_{ref}(F^2) = 0.0558$, $T = 296(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The aerial part of Clausena lansium Lour. Skeels (Rutaceae) were collected and identified by Prof. ZHANG Zhi-Yong (a botanist) of College of Agriculture, Jiangxi Agricultural University, Nanchang, China, in September, 2015. After being crushed into powder (11 kg), the plant material was extracted

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.14 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.12 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14542, 3489, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3289
$N(param)_{refined}$:	279
Programs:	Bruker [1], SHELX [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1698(3)	0.77000(14)	0.69654(10)	0.0256(4)
C2	0.3758(3)	0.74054(14)	0.68935(10)	0.0264(5)
C3	0.4296(3)	0.68691(15)	0.63636(10)	0.0304(5)
H3	0.5666	0.6658	0.6315	0.036*
C4	0.2763(3)	0.66415(15)	0.58956(10)	0.0294(5)
C5	0.0729(3)	0.69661(16)	0.59927(10)	0.0290(5)
C6	0.0137(3)	0.74979(15)	0.65236(10)	0.0302(5)
H6	−0.1233	0.7707	0.6579	0.036*
C7	0.3181(4)	0.61386(17)	0.53044(12)	0.0394(6)
H7	0.4525	0.5913	0.5226	0.047*
C8	0.1666(4)	0.59902(18)	0.48647(12)	0.0418(6)
H8	0.1979	0.5664	0.4484	0.050*
C9	−0.0434(4)	0.63222(16)	0.49657(11)	0.0326(5)
C10	0.5027(3)	0.77553(15)	0.74706(10)	0.0270(5)
H10	0.6245	0.8097	0.7303	0.032*
C11	0.3457(3)	0.84631(15)	0.77615(10)	0.0262(5)
H11	0.3799	0.9060	0.7556	0.031*
C12	0.3363(3)	0.86603(14)	0.84979(10)	0.0245(4)
C13	0.5537(4)	0.89686(16)	0.87190(12)	0.0351(5)
H13A	0.5509	0.9106	0.9178	0.053*
H13B	0.5944	0.9515	0.8481	0.053*
H13C	0.6528	0.8480	0.8637	0.053*
C14	0.1745(4)	0.94127(15)	0.86378(11)	0.0331(5)
H14A	0.0370	0.9185	0.8533	0.050*
H14B	02046	0.9951	0.8376	0.050*
H14C	0.1799	0.9577	0.9092	0.050*
C15	0.1161(3)	0.73046(13)	0.87739(10)	0.0224(4)
H15	0.0101	0.7665	0.8537	0.027*
C16	0.0270(3)	0.69138(14)	0.94019(9)	0.0236(4)
H16	0.1340	0.6540	0.9624	0.028*
C17	−0.1600(3)	0.63008(14)	0.92266(9)	0.0228(4)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H17	−0.2656	0.6675	0.8999	0.027*
C18	−0.0893(3)	0.55166(14)	0.87854(10)	0.0225(4)
H18	0.0043	0.5105	0.9032	0.027*
C19	0.0284(3)	0.58907(14)	0.81909(10)	0.0233(4)
H19	−0.0710	0.6205	0.7899	0.028*
C20	0.1438(4)	0.51497(16)	0.78131(11)	0.0322(5)
H20A	0.0430	0.4704	0.7646	0.039*
H20B	0.2131	0.5435	0.7441	0.039*
O1	−0.0825(2)	0.67877(11)	0.55400(7)	0.0358(4)
O2	−0.1914(3)	0.62388(11)	0.45994(8)	0.0409(4)
O3	0.1374(2)	0.82156(10)	0.75161(7)	0.0268(3)
O4	0.5752(2)	0.70322(11)	0.78821(7)	0.0337(4)
H4	0.4747	0.6770	0.8051	0.051*
O5	0.2937(2)	0.78445(9)	0.89029(6)	0.0238(3)
O6	0.1875(2)	0.65402(9)	0.83914(7)	0.0257(3)
O7	−0.0345(2)	0.76665(10)	0.98124(7)	0.0305(4)
H7A	−0.0835	0.7461	1.0154	0.046*
O8	−0.2503(2)	0.59100(10)	0.97984(7)	0.0318(4)
H8A	−0.3350	0.6277	0.9955	0.048*
O9	−0.2630(2)	0.49892(10)	0.85508(7)	0.0302(4)
H9	−0.3017	0.4627	0.8836	0.045*
O10	0.2956(3)	0.46716(11)	0.81932(9)	0.0431(4)
H10A	0.3979	0.5008	0.8250	0.065*

by refluxing 95% methanol (20 L each) three times. This process yielded methanol-soluble extracts, which were suspended in water and subsequently extracted with PE, EtOAc and *n*-BuOH (3.5 L, each), respectively. The *n*-BuOH part (130 g) was subjected to a reversed-phase column (RP-18) eluting with MeOH-water (10%–100%) to four sub-fractions (A–E). C was subjected to silica gel chromatography (CC) (200–300 mesh) with a gradient system of CH_2Cl_2-MeOH (9:1–7:3, *v*/*v*) to give six fractions C_1–C_6. C_2 was further separated by normal phase silica gel CC (200–300 mesh) with an isocratic system of CH_2Cl_2-MeOH (9:1) to give four fractions $C_{2\text{-}1}$– $C_{2\text{-}4}$. $C_{2\text{-}4}$ was separated by HPLC [H_2O: MeOH (80:20, *v*/*v*)] to afford the title product (10 mg) which was then crystallized from methanol as colorless crystals.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with $U_{iso}(H) = 1.5\ U_{eq}(C)$ for methyl H atoms and 1.2 $U_{eq}(C)$ for all other H atoms. The Flack parameter is not conclusive, thus the absolute configuration can not be retrieved from this diffraction experiment.

Comment

C. lansium Lour. Skeels (*Rutaceae*), belonging to the genus *Clausena* of the family *Rutaceae*, is a fruit tree and a species of strongly scented evergreen tree growing in South China [3, 4]. *Clausena lansium* is famous for their fruits, which are very popular tropical, health-promoting fruits, while their roots, stems, leaves, and seeds have also been extensively applied in folk medicine or traditional Chinese medicine for the treatments of abdominal pain, malaria, cold, dermatopathy, and snake-bites [4, 5]. In our previous research, some coumarins [6, 7] were isolated from some plants of the genus *Clausena*. As a part of our ongoing project towards the discovery of new constituents from the *Clausena* genus, the title compound was extracted and characterized. The compound was obtained as colorless crystals with a blue fluorescence under ultraviolet irradiation (254 nm). It is a dihydrofuranocoumarin with H-2′ and H-3′ in *cis* orientation. In addition, the C-1′ position of this compound was glycosylated and the glycosyl is a *β*-glucose.

In the molecule of the title compound bond lengths and angles within the title structure are very similar to those given in the literature [8]. The molecule consists of two moieties: *β*-glucose and furocoumarin. The pyranose ring of sugar part adopts a chair conformation with all substituents in equatorial positions. The atoms C15, C17 and C19 are coplanar, the atoms C16, C18 and O6 are coplanar, and the dihedral angle of them is 4.15(7)°. The atoms of pyranose ring of furocoumarin part are coplanar. The furanose ring of the furocoumarin part adopts an envelope conformation. This moiety has two chiral centres, at C10 and C11, respectively. The molecular conformation is characterized by the O5-C12-C11-C10, O5-C12-C11-O3, C15-O5-C12-C11, and O6-C15-O5-C12 torsion angles of −58.2°, 68.5°, −54.6°, and 97.9°, respectively. This conformation is stabilized by intramolecular hydrogen bonds.

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References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Editorial Committee of Flora of China, Chinese Academy of Sciences. Flora of China, Science Press: Beijing, China. **43** (1997) 126–127.

4. Arbab, I. A.; Abdul, A. B.; Aspollah, M.; Abdullah, R.; Abdelwahab, S. I.; Ali, M. L. Z.: A review of traditional uses, phytochemical and pharmacological aspects of selected members of Clausena genus (Rutaceae). J. Med. Plants Res. **6** (2012) 5107–5118.
5. Liu, Y. P.; Guo, J. M.; Liu, Y. Y.; Hu, S.; Yan, G.; Qiang, L.; Fu, Y. H.: Carbazole alkaloids with potential neuroprotective activities from the fruits of Clausena lansium. J. Agric. Food Chem. **67** (2019) 5764–5771.
6. Peng, W. W.; Zheng, Y. Q.; Zhao, S. M.; Ji, C. J.; He, W. J.; Tan, N. H.: Coumarins from the roots of Clausena excavata. J. Asian Nat. Prod. Res. **15** (2013) 215–220.
7. Peng, W. W.; Zheng, L. X.; Huo, G. H.: A new furan-coumarin from Clausena lansium. Chem. Nat. Compd. **55** (2019) 440–442.
8. Serda, P.; Grochowski, J.; Duddeck, H.: The structure of marmesinin by powder and single-crystal diffraction methods. J. Alloys Compd. **362** (2004) 224–230.