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Supramolecular Architectures of 2-(3-(4-acetoxyphenyl)propanoyl)benzene-1,3,5-triyl triacetate (1) and 4-(3-(4-acetoxyphenyl)propanoyl)-5-hydroxy-1,3-phenylene diacetate (2)

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Abstract

2-(3-(4-acetoxyphenyl)propanoyl)benzene-1,3,5-triyl triacetate (**1**), $C_{25}H_{22}O_9$ and 4-(3-(4-acetoxyphenyl)propanoyl)-5-hydroxy-1,3-phenylene diacetate (**2**), $C_{21}H_{20}O_8$ were formed via esterification of phloretin and acetic anhydride, respectively. Their structures all reveal three-dimensional framework structures. In (**1**), the molecule, which contains two intramolecular O···O interactions, is existed as dimer that forms classic cyclic $R^2_2(9)$ C-H···O hydrogen bonding interactions. The molecules are linked by a combination of C-H···O and C-H···π(arene) hydrogen bonds. It is interesting that two molecules of the dimer occur different intermolecular interactions. In (**2**), several weak C-H···O interactions of the types Caryl-H···O, C_{sp^3}-H···O and intramolecular hydrogen bond O-H···O are present. Both molecules give cyclic $R^2_2(4)$ motif. These hydrogen bonds and interactions appear to play an important role in controlling the molecular conformation.

Keywords

Phloretin Derivatives, Crystal Structure, Hydrogen Bonds

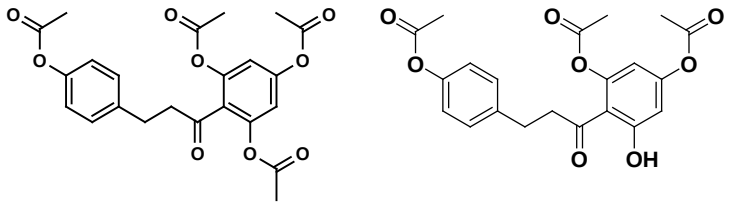
1. Introduction

Phloretin [2',4',6'-trihydroxy-3-(4-hydroxyphenyl)-propiophenone] is a polyphenolic known by its anti-oxidant activity and it is mainly found in apples. Besides its potential antioxidant property, the anti-allergic, anti-inflammatory, antimicrobial and anti-cancer activity of phloretin have attracted the attention of food

manufacturers and consumers [1] [2] [3] [4]. Meanwhile, the benefits of phloridzin or other phloretin derivatives for human health are well documented by a number of publications and patents. Most of these relate to diabetes, obesity, stress hyperglycemia, membrane permeability and longevity-extending agents in foods, beverages, food additives, pharmaceuticals and cosmetics [5]-[10]. In order to be in compassion with the phloretin, two acetylation products of phloretin(2-(3-(4-acetoxyphenyl)propanoyl)benzene-1,3,5-triyl triacetate (**1**), $C_{25}H_{22}O_9$ and 4-(3-(4-acetoxyphenyl)propanoyl)-5-hydroxy-1,3-phenylene diacetate (**2**), $C_{21}H_{20}O_8$, cf. Scheme 1, Figure 1 and Figure 2) were synthesized and recrystallized from dichloromethane that are suitable for x-ray diffraction.

2. Molecular Structure

In (**1**), the molecule, which contains two intramolecular O···O interactions, is existed as dimer. Each of the molecules exhibits a strong intramolecular interaction of O···O type (Figure 3), the distances O7/O4 and O16/O13 being 2.875 and 2.822 Å, respectively. The intramolecular hydrogen bonds provides two distorted envelop $R_{11}(5)$ rings, O7 and O16 as flap folded upward the mean plane of 0.909 Å and 0.847 Å. This presumably sets the stage for the interactions observed within the crystal lattice. The crystallographic data are presented in Table 1.



Scheme 1. Compounds **1** and **2**.

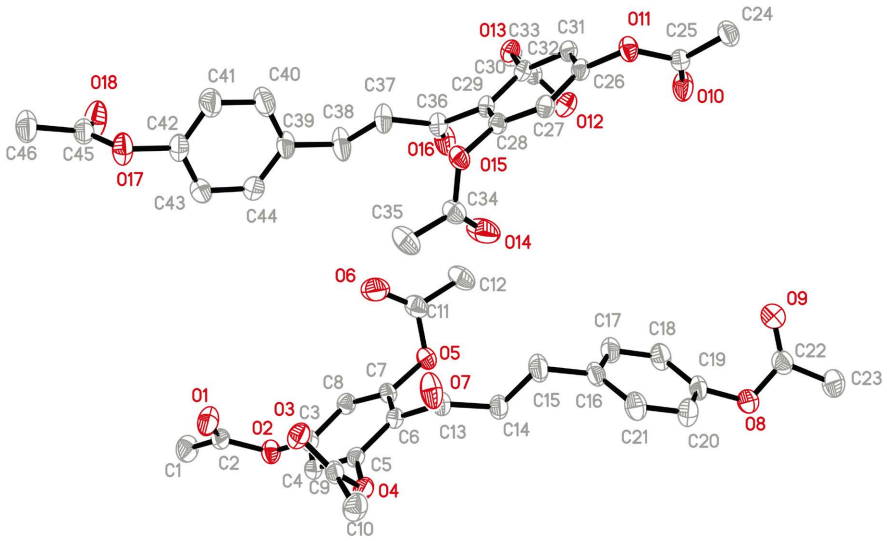


Figure 1. Anisotropic ellipsoid representation of the compound **1** together with atom labelling scheme. The ellipsoids are drawn at 30% probability level, hydrogen atoms are shown as spheres of arbitrary radi.

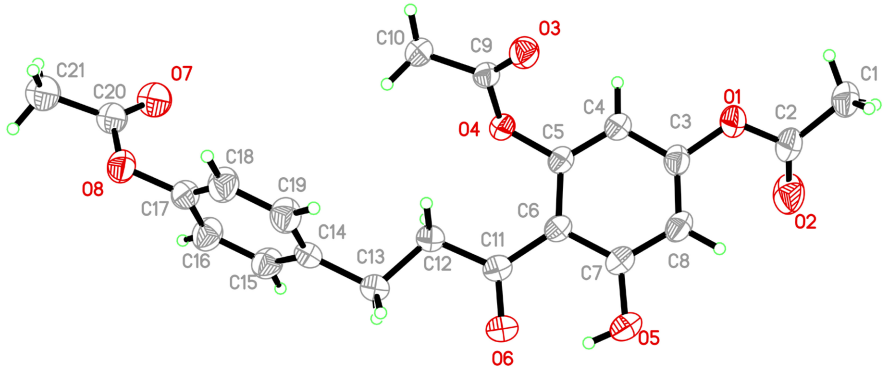


Figure 2. Anisotropic ellipsoid representation of the compound **2** together with atom labelling scheme. The ellipsoids are drawn at 30% probability level, hydrogen atoms are shown as spheres of arbitrary radi.

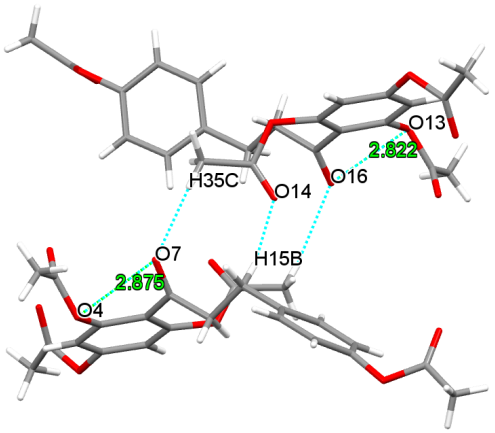


Figure 3. The crystal structure of compound I, showing the formation of hydrogen bonds O···O and C-H···O, Hydrogen bonds are shown as dashed lines.

Table 1. Crystal data, data collection and structure refinement.

Compound	1	2	Compound	1	2
Formula	$C_{23}H_{22}O_9$	$C_{21}H_{20}O_8$	Reflections:		
Formula weight	442.41	400.37	Collected	21,843	5040
Crystal system	Monoclinic	Triclinic	Unique (Rint)	7810	3528
Space group	P21/c	P-1	With $I > 2\sigma(I)$	5179	2665
a (A˚)	10.4343(7)	8.2007(16)	Number of parameters	586	267
B (A˚)	19.9379(13)	8.9510(17)	R (F) [$I > 2\sigma(I)$]	0.0498	0.0415
c (A˚)	21.1546(14)	14.047(3)	wR (F^2) [$I > 2\sigma(I)$]	1.1477	0.1143
V (A˚^{3})	4383.9(5)	999.4(3)	R (F) [all data]	0.0787	0.0543
Z	8	2	wR (F^2) [all data]	1.1489	0.1248
Dx (g·cm^{-3})	1.341	1.330	Goodness of fit	1.044	1.047
Crystal size (mm)	0.37 × 0.28 × 0.19	0.39 × 0.33 × 0.25	F (000)	1856	420
hkl range	−12 ≤ h ≤ 9 −23 ≤ k ≤ 17 −25 ≤ l ≤ 24	−9 ≤ h ≤ 9 −10 ≤ k ≤ 9 −16 ≤ l ≤ 15			

The molecules of (**1**) are linked into sheets by a combination of the types Caryl-H···O, C_{sp^3}-H···O and C_{sp^3}-H···π hydrogen bonds. Although there are many O atoms in the molecule of (**1**) potentially available as hydrogen-bond acceptors, not at all O atoms in fact play part in the hydrogen bond. Instead, atom O14 acts as a triple acceptor of hydrogen bonds, and atoms O7 and O16 act as a double acceptor of hydrogen bonds.

In (**1**), unconventional benzene ring-carbonyl C8-H8···$O9^{i}$ hydrogen bonding favors the formation of one-dimensional chains, the axes of which run parallel to [100]. Similar one-dimensional chains are observed in the crystal structure of 1,4-phenylenediammonium bis(hydrogen phthalate) [11]. Molecules in adjacent chains (along a axis) are held together by weak types Caryl-H···O, C_{sp^3}-H···O and C_{sp^3}-H···π interactions to form supramolecular. Molecules are arranged in zigzag chains along the c axis and are held together by weak C_{sp^3}-H···O hydrogen bonds between atom H8A of the methoxy group and the carbonyl O atom of a neighbouring molecule.

The molecules of compound 2 exist in O-H···O and C-H···O hydrogen bonds (**Table 2**), by which molecules are linked into three-dimensional framework structures. The dihedral angle between two benzene rings is 67.15˚. But in (1) the dihedral angle (77.25˚ and 47.27˚ respectively) between two benzene rings in one molecule is strikingly different from the other. The torsion angles of C5-O4-C9-O3 are 5.7(3)˚ (**Table 3**). Two intermolecular hydrogen bonds C1-H1C···$O5^{i}$ and C4-H4···$O6^{i}$ [symmetry codes: (i) x-1, y, z] which connect the molecule in adjacent unit cells to form infinite long chains along the b-axis are observed (cf. **Figure 4**). Carbonyl C11=O6 is almost planar with the mean of benzene ring from C3 to C8, the maximum deviations from the mean plane through the non-H atoms are 0.094 A˚ for atom O6. While in the crystal of dimer (**1**) carbonyl C13=O7 is obviously unplanar with the mean of benzene ring from C3 to C8 in one molecular, so is the other molecular (**Table 4**). The deviations from the mean plane (C3-C8) through the non-H atoms which are 0.955 A˚ for atom O7 and from the mean plane (C26-C31) through the non-H atoms which are 0.812 A˚ for atom O16 are by far larger than 0.094 A˚ in (**2**).

3. Crystal Packing

There are also some important differences in the crystal packing of compound **1** (cf. **Figure 5**). The molecules **1** is abundant with the good hydrogen bond acceptors

Table 2. Hydrogen bond data of compound **2**.

D	H	A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(˚)
O5	H5	O6	0.82	1.78	2.505(3)	146.4
C12	H12B	O3	0.97	2.48	3.389(3)	156.8
C18	H18	O1	0.93	2.60	3.510(4)	167.3
C1	H1C	O5	0.96	2.61	3.539(3)	163.8

Table 3. Selected geometrical parameters for **2** (Å, °) with esd's in parentheses.

O1-C2	1.381(3)	C2-O1-C3	121.7(2)
O2-C2	1.192(4)	C9-O4-C5	119.10(17)
C1-C2	1.485(4)	O2-C2-O1	122.5(3)
C11-O6	1.236(3)	C5-O4-C9-O3	5.7(3)
O1-C2-C1	109.9(3)	C3-O1-C2-O2	11.6(4)
C8-C3-C4	121.7(2)	C5-O4-C9-C10	−173.6(2)
C8-C3-O1	123.1(2)	C17-O8-C20-O7	1.0(4)
C4-C3-O1	115.0(2)	C17-O8-C20-C21	−178.3(2)

Table 4. Selected geometrical parameters for **1** (Å, °) with esd's in parentheses.

O1-C2	1.188(3)	H10A-C10-H10C	109.5
O2-C2	1.374(3)	C14-C15-H15A	108.9
C1-C2	1.472(4)	C3-O2-C2-O1	−3.8(3)
C13-O7	1.209(3)	C3-O2-C2-C1	175.1(2)
C2-O2-C3	117.62(18)	O7-C13-C14-C15	−29.5(4)
O1-C2-O2	121.7(2)	C13-C6-C7-O5	6.5(3)
O3-C9-C10	127.7(2)	C22-O8-C19-C18	66.6(3)

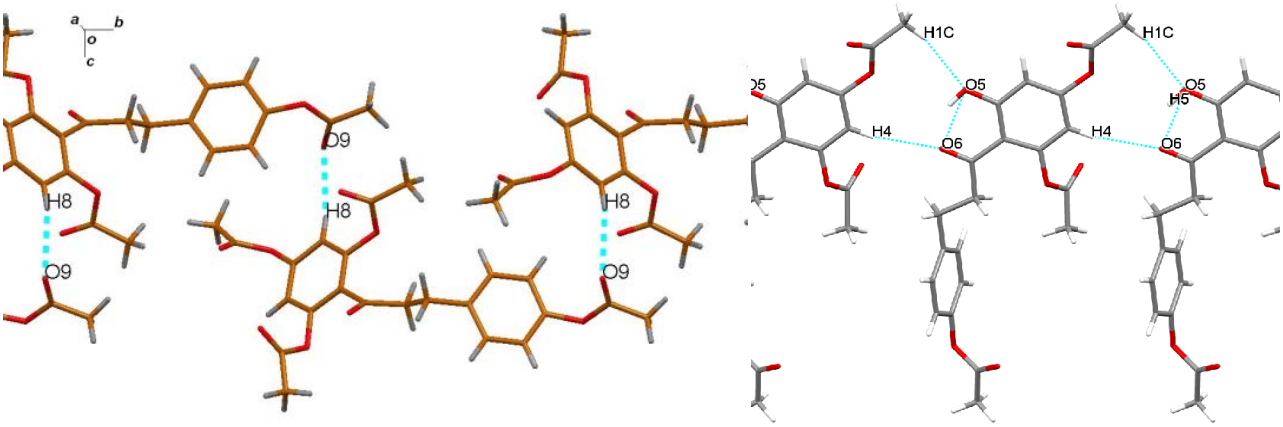


Figure 4. The hydrogen bonded chains of molecules **1** and **2** as seen approximately along a and b axis respectively. Hydrogen bonds are shown as dashed lines.

and the good hydrogen bond donor- C=O group-form many hydrogen bonds and contacts. The crystal packing is mostly caused by the interplay of van der Waals, stacking and weak hydrogen bonding interactions. The crystal packing of compound **2** (cf. **Figure 6**) shows that the molecules connect each other by means of C-H···O hydrogen bonds. These chains are then connected by weaker contacts (C-H···O) into three-dimensional crystal structure.

Diffraction data for I and II were collected at room temperature by the ω-scan technique on an Agilent Technologies Xcalibur four-circle diffractometer with Bruker SMART CCD Eos CCD-detector and graphite-monochromatized MoKa

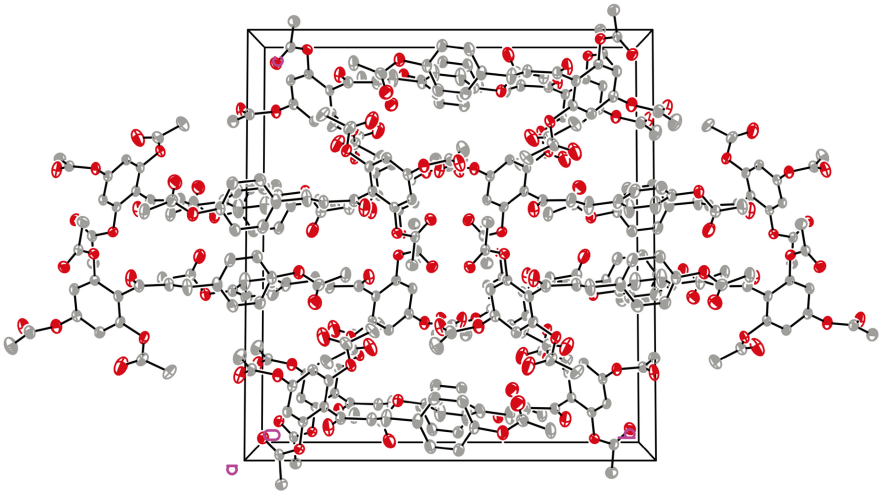


Figure 5. Crystal packing of compound **1** as seen along a-axis.

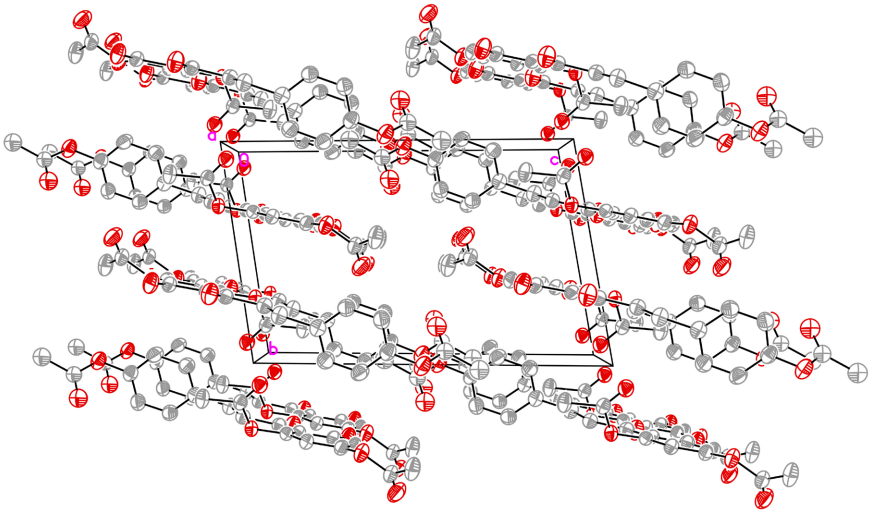


Figure 6. Crystal packing of compound **2** as seen along a-axis.

radiation source (k = 0.71073 A˚). The data were corrected for Lorentz-polarization as well as for absorption effects. The calculations were mainly per-formed within the WinGX program system [12]. The structure was solved with SIR92 [13] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [14]. The scattering factors incorporated in SHELXL97 were used. The function $\Sigma(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w - 1 = [\delta^2(F_o)^2 + (A \cdot P)^2 + B \cdot P](P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were placed geometrically in idealized positions and refined as rigid groups with their Uiso's as 1.2 times Ueq of the appropriate carrier atom. Relevant crystal data are listed in Table 1, together with refinement details. Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cam-bridge Crystallographic Data Centre, Nos. CCDC-1432985 (**1**), and CCDC-1432986 (**2**). Copies of this information 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 website: http://www.ccdc.cam.ac.uk/.

4. Conclusion

In this paper, we synthesized and recrystallized two acetylation product of phloretin(2-(3-(4-acetoxyphenyl)propanoyl)benzene-1,3,5-triyl triacetate (1), $C_{25}H_{22}O_9$ and 4-(3-(4-acetoxyphenyl)propanoyl)-5-hydroxy-1,3-phenylene diacetate (2), $C_{21}H_{20}O_8$ that were suitable for x-ray diffraction. Their structures all reveal three-dimensional framework structures, which contain intramolecular O···O interactions, C-H···O, C-H···π(arene) and O-H···O hydrogen bonds, several weak C-H···O interactions of the types Caryl-H···O, C_{sp}^3-H···O, and give cyclic $R^2_2(9)$ and $R^2_2(4)$ motif. These hydrogen bonds and interactions appear to play an important role in controlling the molecular conformation and activity.

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Conflicts of Interest

The authors have no conflicting interests to declare.

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