International Journal of Applied Research 2016; 2(9): 470-473

ISSN Print: 2394-7500
ISSN Online: 2394-5869
Impact Factor: 5.2
IJAR 2016; 2(9): 470-473
www.allresearchjournal.com
Received: 06-07-2016
Accepted: 07-08-2016

Bandhan Sharma
Department of Physics, Govt. P.G. College for Women Parade (Autonomous), Jammu and Kashmir, India

Correspondence
Bandhan Sharma
Department of Physics
Govt. College for Women parade (Autonomous)
Jammu, Jammu and Kashmir, India

Comparative crystallographic x-ray analysis of three photoactive furanocoumarins

Bandhan Sharma

Abstract
The molecular and crystal structure of imperatorin, phellopterin and rutaretin have been determined by using crystallographic and computational techniques. The compound of imperatorin crystallizes in triclinic space group $P\bar{1}$ with unit cell parameters a=11.1150(10)Å, b=11.8240(10)Å, c=11.9290(10)Å, α=64.90(1)°, β=83.53(1) °, γ=89.25(1) °. The compound of phellopterin crystallizes in triclinic space group P1with unit cell parameters a=8.431(3)Å, b=8.947(3)Å, c=11.125(4)Å, α=64.11(5)°, β=71.13(5) °, γ=78.04(5) °. The compound of rutaretin crystallizes in monoclinic space group C2 with unit cell parameters a=24.616(8)Å, b=8.186(3)Å, c=6.632(2)Å, β=103.99(2) °. The number of molecules per unit cell is 4 for imperatorin and rutaretin and 2 for phellopterin. The crystal structure of imperatorin has two asymmetric molecule whereas phellopterin and rutaretin have one asymmetric molecule. The final R-factor for (imperatorin) is 0.0431, (phellopterin) 0.0592 and (rutaretin) 0.0356. All the three molecules exhibit intra and inter C-H...O hydrogen bonding. A comparative crystallographic analysis of these three photoactive furanocoumarins is reported in this paper.

Keywords: Furanocoumarins, photoactive, x-ray diffraction, pyrone ring, hydrogen bonding

1. Introduction
The photochemical behaviour in furanocoumarins is generally attributed to the carbonyl stretching (C=O) in the pyrone moiety of coumarin nucleus [1]. The derivatives of coumarins usually occur as secondary metabolites present in seeds, roots and leaves of many plant species. Their function is far from clear, though suggestions include waste products, plant growth regulators, fungistats and bacteriostats [2]. It is, therefore, of utmost importance that the synthesis of coumarin and its derivatives should be achieved by a simple and effective method. A wide spectrum of biological activity of coumarin compounds is known, e.g., antithrombotic effect, vasodilating effect on vessel, reduction on blood pressure, antispastic and photosensitising effect [3].
The compound of imperoterin was isolated by column chromatography using silica gel and n-hexane. Several fractions were collected. The fractions eluted with n-hexane: EtoAc (9:1) mixture gave a fluorescent compound homogeneous on TLC plate, further purified by preparative TLC. Recrystallized from MeOH yielded plate yellow crystals (50mg) identified as imperoterin on the basis of UV, IR, NMR ans Mass [4-5]. In present study phellopterin has been isolated from the roots of *Heracleum thomsoni* from Leh and Ladakh Region of Jammu and Kashmir State of India [6]. Dried and powdered roots (2kg) of Heracleum thomsoni were extracted with petroleum ether in a soxhlet extraction apparatus for 24 hour. The extract was concentrated and residue (60g) was chromatographed over deactivated alumina (1kg) containing 10% water. Elution was started with petroleum ether followed by mixture of petroleum ether and ethyl acetate.
Phellopterin was obtained from petroleum ether: ethyl acetate (9:1) eluate on repeated crystallization. In the present study third molecule rutaretin has been isolated from the seeds of Apium graveolens, a weed cultivated in several parts of India [7]. The seeds of this plant are valuable flavouring agents and are widely used in the Ayurvedic and Unani system of medicines for the treatment of bronchitis, asthma and also as household remedy for rheumatism and gout [7].

Dried and powdered seed of Apium graveolens were extracted with petroleum ether which was chromatographed over a column of silica gel. Elution with ethyl acetone yielded a compound having yellow fluorescence in UV light. The structure identified as rutaretin on the basis of UV, IR and NMR [8]. The chemical structures of all the three molecules are present in Figure 1.

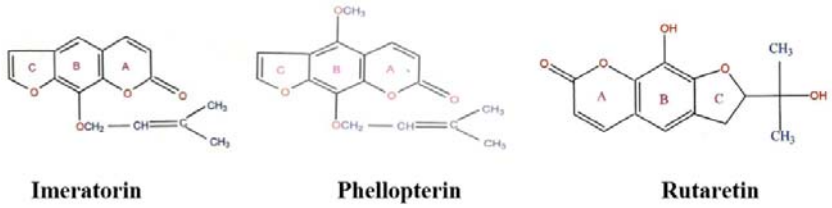

Fig 1: Chemical structures of the molecules

2. Experimental Section

The single crystals of compounds were obtained by slow evaporation technique using n-hexane, mixture of acetone and petroleum ether and acetone as solvents. A transparent needle shaped single crystal of all three compounds with dimensions (0.3×0.1×0.1)mm was mounted on the Enraf-Nonius CAD-4 diffractometer for automatic intensity data collection by using MoKα radiation (λ=0.71.73 Å). ω/2θ scan mode was employed for the data collection with θ-range (4.01 to 69.94º) for imperoterin, (2.04 to 28.23º) for phellopterin and (2.14 to 24.96 º) for rutaretin. The compound crystallizes in the triclinic space group P1 with unit cell parameters: a=8.431(3) Å, b=8.947(3) Å, c=11.125(4) Å, α =69.11(5)º,β=71.13(5)º and γ=78.04(5)º, Z=2, V=737.9(4) Å^3. A total of 5926 reflections were recorded in case of imperatorin and out of which 5350 were found to be unique (0≤h≤13, -14≤k≤14, -14≤l≤14),and 4657 were considered to be observed [Fo>4σ(Fo)]. In case of phellopterin 6087 reflections were recorded and out of which 2586 were found to be unique (-10≤h≤11, -11≤k≤11, -14≤l≤14), 2549 were considered to be observed [Fo>4σ(Fo)]. In case of rutaretin 4258 reflections were recorded and out of which 2379 were found to be unique (-35≤h≤36, -11≤k≤12, -9≤l≤9), 2216 were considered to be observed [Fo>4σ(Fo)]. The reflection data of all three compounds were collected for Lorentz and polarization effects and no absorption correction was applied. The structures of all three compounds were determined by SHELXS97 Software [9]. Full matrix least square refinement of all non-hydrogen atoms including their corresponding thermal parameters was carried out using SHELXL97 software [10]. The final cycle of refinement with anisotropic thermal parameters for non-hydrogen atoms converged R-factor at 0.0431 for imperoterin, 0.059 for phellopterin and 0.0356 in case of rutaretin. Atomic scattering factor were taken from International Tables for Crystallography (1992, Vol. C Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are listed in Table 1.

Table 1: Crystal data and structure refinement details.

	Imeratorin	**Phellopterin**	**Rutaretin**
Crystal description	**Transparent needles**	**Transparent needles**	**Transparent needles**
Empirical formula	$C_{16}H_{14}O_4$	$C_{17}H_{16}O_5$	$C_{14}H_{16}O_6$
Formula weight	270.27	300.3	280.27
Crystal size (mm)	0.3×0.1×0.1	0.3×0.1×0.1	0.3×0.1×0.1
Wavelength	1.54178 Å	0,71073 Å	0.71070
Unit cell dimensions	a=11.1150(10)Å,	a=8.431(3)Å,	a=24.616(8)Å,
	b=11.8240(10)Å,	b=8.947(3)Å,	b=8.186(3)Å,
	c=11.9290(10)Å,	c=11.125(4)Å,	c=6.632(2)Å,
	α=64.90(1)°,	α=64.11 (5)°,	
	β=83.53(1) °,	β=71.13(5) °	β=103.99(2) °
	γ=89.25(1) °	γ=78.04(5) °	
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P$\bar{1}$	P1	C2
Volume	1409.6(2) Å^3	737.9(4) Å^3	1296.7(7) Å^3
Z, Calculated density	4, 1.274 Mg/m^3	2, 1.352 Mg/m^3	4,1.436 Mg/m^3
F(000)	568	316	592
Index ranges	0 ≤ h≤ 13,	-10 ≤ h ≤ 11,	-35 ≤ h ≤ 36,
	-14 ≤ k ≤14,	-11 ≤ k ≤ 11,	-11 ≤ k ≤ 12,
	-14 ≤ l ≤ 14	-14 ≤ l ≤ 14	-9 ≤ l ≤ 9
Reflections collected	5926	6087	14258
Reflections unique	5350	2586	2379
Goodness-of-fit on F2	1. 052	1.198	1.081
R-factor	0.0431	0.059	0.0356
Largest diff. Peak and hole	0.23 and -0.16 eÅ^{-3}	0.20 and -.26 eÅ^{-3}	0.41and-0.28 eÅ^{-3}

3. Results and Discussion

The bond distances for non-hydrogen atoms in the pyrone moiety of all molecules are presented in Table 2. An ORTEP view of all three molecules with atomic numbering scheme [11] is in Figure 2. The geometrical calculations were performed by using PARST [12] and PLATON [13]. The bond

distances and angles are in good agreement with the values reported for some analogous structures [14-18]. The magnitude of torsion angle C9-O17-C18-C19 present in the prenyloxy side chain located at atom C9 is 176.9(2)º (molecule-I) and 62.2(2)º (molecule-II) in case of imperoterin, 174.3(2) º in case of phellopterin and 178.4(12) º for rutaretin. However this value is in good agreement with the corresponding values reported for related furanocoumarins [14-16] except for molecule-II of imperatorin.

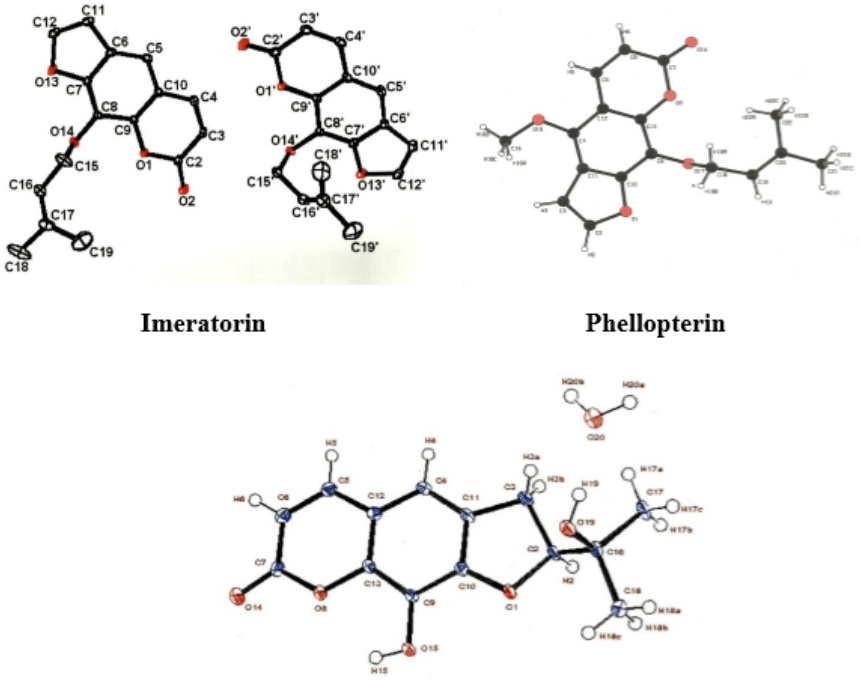

Fig 2: ORTEP view of all the three molecules with displacement ellipsoids drawn at the 50% probability level

The pyrone ring of all the molecules is perfectly planner with maximum deviation of 0.009(2) Å. In case of imperotrin, the bifurcated acceptor O2 is involved with two intermolecular interactions in molecule-I whereas in molecule-II, it makes one intermolecular and one intramolecular interaction. Atoms C4 and C12 act as donor atoms in all the above mentioned weak interactions. The molecules of phellopterin are linked by paired C-H...O hydrogen bonds into C(6) graph set, where C refers to chain [19]. The molecules are linked to one another through C-H...O hydrogen bonds and hydrogen-bonding network is shown in Figure 3. The C2-H2...O14 and C5-H5...O1 intermolecular hydrogen interactions result into a linear chain like configuration. In intermolecular C2-H2...O14 interaction, C2 at (x, y, z) acts as hydrogen donor to O14 at (-1+x, 1+y, z) where as in case of C5-H5...O1 intermolecular interactions, O1 at (1+x, y, z) acts as hydrogen acceptor. The C-H...O linear chains packed along bc-plane over different layers of molecule depicts the supramolecular structure of phellopterin. The hydroxyl-methylethyl chain located at C2 of rutaretin is inclined more towards O1(108.4 º) than C3 (114.9 º) which might be the reason for the formation of C18-H18...O1 intermolecular interaction. Both the hydroxyl groups of the molecule located at C9 and C16 are linked through a linear intermolecular hydrogen bond O15-H15...O19 at (-x, y, 2-z) in which O19 acts as proton acceptor. All hydrogen interactions fall in the range of weak interactions as suggested by Desiraju and Steiner [20]. The geometry of C-H...O hydrogen bonds is presented in Table 3.

4. Conclusion

The photoactivity of furanocoumarins is due to the carbonyl stretching (C=O) in the pyrone moiety of coumarin nucleus. The average value of bond distances C2=O2 and C3=C4 in the pyrone ring of coumarin moiety for all the three coumarin structure taken in this work are 1.211 and 1.34 Å, respectively, and these bond distances are responsible in the photoactivity of these coumarins. The geometry of hydrogen bonds of all the three structures fall in the range of weak interactions.

Table 2: Bond distances for non hydrogen atoms of the pyrone moiety.

Imeratorin			
O1-C2	1.381(2)	O1′-C2′	1.386(2)
C2-O2	1.209(2)	C2′-O2′	1.208(2)
C2-C3	1.438(3)	C2′-C3′	1.433(3)
C3-C4	1.337(3)	C3′-C4′	1.336(3)
C4-C10	1.4441(2)	C4′-10′	1.443(2)
C9-C10	1.403(2)	C9′-C10′	1.402(2)
O1-C9	1.386(2)	O1′-C9′	1.380(2)
Phellopterin		**Rutaretin**	
O8-C13	1.373(2)	O8-C13	1.387(15)
C12-C13	1.401(2)	C12- C13	1.406(19)
C5-C6	1.329(3)	C5-C6	1.358(2)
C5-C12	1.433(2)	C5-C12	1.429(2)
C6-C7	1.435(3)	C6-C7	1.229(16)
C7-O14	1.198(3)	C7-O14	1.368(18)
C7-O8	1.385(2)	C7-O8	1.358(2)

Table 3: Geometry of C-H...O hydrogen bonds.

C-H...O	H...O(Å)	C...O(Å)	C-H...O(º)
Imeratorin			
C4-H4...O2′	2.54	3.34	137.8
C4′-H4′...O2	2.58	3.46	159.7
C11-H11...O14′	2.64	3.35	139.3
C12-H12...O2	2.36	3.27	172.4
C12′-H12...O2′	2.34	3.32	178.8
Phellopterin			
C2-H2...O14	2.41	3.16	137.5
C5-H5...O1	2.59	3.30	133.7
Rutaretin			
C18-H18...O1	2.84	3.38	142.4
O15-H15...O19	2.64	3.47	168.5
O20- 20A...O14	2.28	3.31	171.3

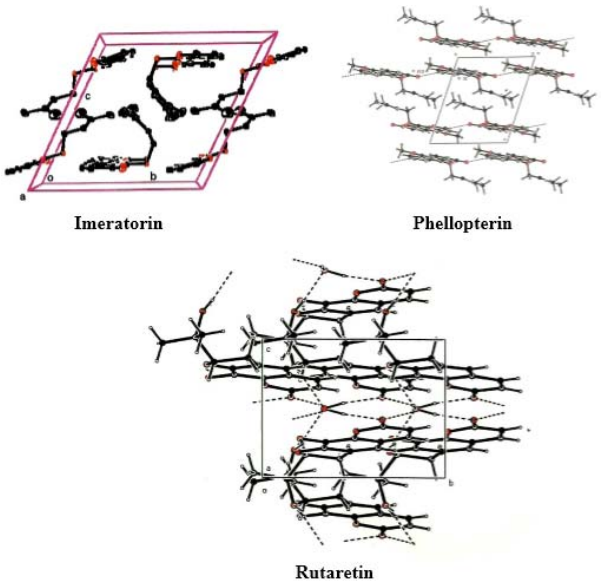

Fig 3: C-H...O hydrogen-bonding network.

5. References

1. Musajo L, Rodighiero G. Herb Hungarica. 1979; 19:79.
2. Singh V, Singh J, Kaur P, Kad GL. Journal of Chemical Research. 1997, 58.
3. Wolska I, Borowiak T, Gawron M. Acta Crystallography. 1990; C46:2146.
4. Shawl AS, Raina VK, Kumar T, Srivastava SK, Kumar S. Journal of Medical and Arom. Plant Sciences. 1998; 20:722.
5. Duddeck H, Elgamol MHA, Abdethay FK. Tetrahedron. 1980; 35:13.
6. Gupta BD, Banerjee SK, Handa KL, Atal CK. Indian Journal of Chemistry. 1978; 16B:38.
7. Garg SK, Gupta SR, Sharma ND. Phytochemistry. 1978; 17:2135.
8. Gupta BD. Private communications RRL Jammu. 2004; 1:32.
9. Sheldrick GM. SHELXS97, Program for crystal structure determination, University of Gottingen, Federal Republic of Germany. 1997.
10. Sheldrick GM. SHELXL97, Program for refinement of crystal structures, University of Gottingen, Federal Republic of Germany. 1997.
11. Farrugia LJ. Journal of Applied Crystallography. 1997; 30:565.
12. Nardelli M. Journal of Applied Crystallography. 1995; 28:659.
13. Speck AL. PLATON for Windows, University of Ultrecht, The Netherlands. 1999.
14. Sharma B. Indian Journal of pure and applied Physics. 2015; 53:808-812.
15. Rajnikant, Dinesh, Shawl AS, Singh TP, Sharma B. Journal of Chemical Crystallography. 2005; 35(11):913.
16. Rajnikant, Dinesh, Mousmi, Varghese B, Sharma B. Indian Journal of Physics. 2005; 79(1):73.
17. Rajnikant, Dinesh, Kamni, Sharma B. Ind Journal of Pure and Applied Physics. 2004; 42:524.
18. Rajnikant, Gupta VK, Singh A, Lal M. Journal of Molecular Materials. 1996; 6:199.
19. Berstein J, Etter MC, Leiserowitz L, Burgi HB, Dunitz JD. (Weinheim: VCH). 1994; 2:431.
20. Desiraju GR, Steiner T. The weak hydrogen bond in Structural Chemistry and Biology, IUCr, Oxford Press. 1999, 48.