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Synthesis, Characterization and Spectral Investigation of 3-Benzoyl-6-Chloro-2-(4-Chlorophenyl)Chroman-4-One

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Abstract
The present work describes the synthesis and structural characterization of a substituted chroman-4-one derivative, namely 3-benzoyl-6-chloro-2-(4-chlorophenyl)chroman-4-one [3-I(a)]. The compound was synthesized through the reaction of 1-(5-chloro-2-hydroxyphenyl)-3-phenylpropane-1,3-dione [2-I] with 4-chlorobenzaldehyde in absolute ethanol using piperidine as a basic catalyst. The reaction mixture was refluxed for 15–20 min, followed by acidification with dilute hydrochloric acid. The separated product was purified by crystallization from an ethanol–acetic acid mixture. The synthesized compound was obtained as a light-yellow crystalline solid in 76% yield, with a melting point of 148 °C. Its identity and structural features were investigated by physical examination, TLC, elemental analysis, mass spectrometry, infrared spectroscopy and proton nuclear magnetic resonance spectroscopy. The molecular formula was assigned as $C_{22}H_{14}Cl_2O_3$, with a calculated molecular mass of approximately 396.9 g mol^{-1}. The mass spectrum displayed the characteristic chlorine isotope cluster around m/z 397–400, together with diagnostically important fragment ions at m/z 361.91, 291.63, 105.21 and 77.23. The IR spectrum exhibited absorptions attributable to aromatic and aliphatic C–H stretching, carbonyl groups, aromatic C=C stretching and the cyclic C–O–C functionality. The ^{1}H NMR spectrum showed two characteristic doublets at δ 5.38 and 6.04 ppm with J = 11 Hz, assigned to H-2 and H-3 of the chromanone ring, respectively. The combined analytical and spectroscopic observations support the proposed structure of the synthesized compound.

***Keywords**: Chroman-4-one, benzoyl group, chlorinated flavanone, synthesis, IR spectroscopy, ^{1}H NMR, mass spectrometry, spectral characterization.*

1. Introduction

Heterocyclic and oxygen-containing aromatic compounds constitute an important area of synthetic organic chemistry because of their structural diversity and broad chemical applications. Among oxygen-containing heterocycles, chromanones and related flavonoid-type systems have attracted considerable interest because their molecular frameworks provide useful platforms for the development of structurally diverse derivatives. Flavonoid-related compounds comprise several structural classes, including flavanones, flavones, flavonols, chalcones and related oxygen heterocycles. These compounds occur naturally and have also been extensively investigated through synthetic approaches.

The basic flavonoid framework contains a C_6–C_3–C_6 carbon skeleton, while structural modification of the aromatic rings and heterocyclic portion produces a wide range of derivatives. Flavanones are characterized by a partially saturated oxygen-containing heterocyclic ring and are important intermediates in flavonoid chemistry. Reviews of flavonoid chemistry have described the occurrence, identification, synthesis and biological significance of flavanones and related compounds (Veitch & Grayer, 2008). More recent studies have continued to investigate synthetic modification of flavonoid and chalcone systems because changes in substitution patterns can significantly alter their physicochemical properties and potential biological behaviour.

Synthetic transformations involving substituted aromatic aldehydes and 1,3-dicarbonyl compounds provide useful routes toward oxygen heterocycles. The presence of an ortho-hydroxy group in an aromatic precursor facilitates intramolecular cyclization, leading to chromanone or flavanone-type structures. Depending on the reaction conditions and the structures of the starting materials, different cyclization products can be formed, making reaction conditions important in controlling product formation (Mocanu et al., 2023).

Spectroscopic techniques are particularly valuable for establishing the structures of newly synthesized organic compounds. Infrared spectroscopy provides information about characteristic functional groups through their vibrational absorptions. The mid-infrared region is commonly

used for identifying functional-group vibrations and structural features. Proton nuclear magnetic resonance spectroscopy is one of the principal methods used for determining the chemical environment and connectivity of hydrogen atoms in organic molecules. Mass spectrometry provides molecular-mass information and fragmentation patterns that are useful for supporting molecular-formula assignments and structural interpretation.

The objective of the present study was therefore to synthesize 3-benzoyl-6-chloro-2-(4-chlorophenyl)chroman-4-one [3-I(a)] and to establish its proposed structure using physical properties, chromatographic behaviour, elemental analysis and spectroscopic techniques.

2. Literature Review

Flavonoids and related oxygen heterocycles represent an extensively investigated family of natural and synthetic compounds. The literature describes flavanones as important members of the flavonoid family and as intermediates in the synthesis of structurally related compounds. Naturally occurring flavonoids include flavones, flavanones, flavonols, chalcones, anthocyanins and several other subclasses (Veitch & Grayer, 2008).

Synthetic chemistry has provided numerous approaches to flavonoid skeletons. Condensation reactions involving appropriately substituted aromatic carbonyl compounds followed by cyclization constitute important routes to these systems. Chalcones and related α,β-unsaturated carbonyl compounds can undergo cyclization under suitable conditions to produce oxygen-containing heterocyclic systems. The synthetic behaviour of such substrates depends on substituents, catalysts, solvents and reaction conditions.

The structural modification of flavonoid frameworks is also an active research area. Substitution with halogen atoms, methoxy groups, benzoyl groups and other aromatic substituents can modify molecular polarity, electronic distribution, lipophilicity and spectral properties. Consequently, systematic synthesis and characterization of substituted derivatives remains useful for understanding structure–property relationships.

Modern spectroscopic characterization is essential in this field. FT-IR spectroscopy is particularly useful for identifying carbonyl, C–O–C, aromatic C–H and aromatic C=C functionalities. Proton NMR gives information regarding the number and environment of hydrogen atoms and allows coupling relationships to be examined. Mass spectrometry provides molecular-ion and fragment-ion information, with isotope patterns being especially useful for compounds containing chlorine or bromine.

The present compound contains two chlorine atoms, one attached to the chromanone aromatic ring and another attached to the pendant phenyl ring. Therefore, its mass spectrum is expected to show a characteristic chlorine isotope distribution. The combination of these analytical methods provides a multidimensional approach to structural confirmation.

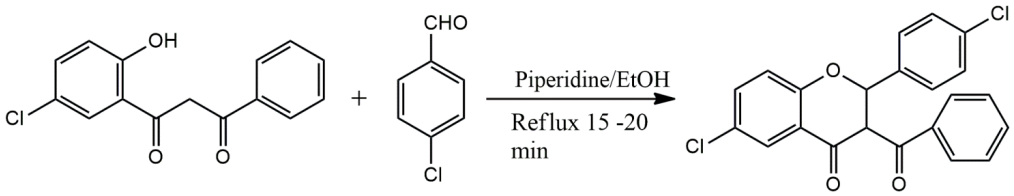
3. Research Work

3.1 Materials and reagents

The starting material 1-(5-chloro-2-hydroxyphenyl)-3-phenylpropane-1,3-dione [2-I], 4-chlorobenzaldehyde, absolute ethanol, piperidine, dilute hydrochloric acid and an ethanol–acetic acid crystallization mixture were used in the synthesis. Analytical-grade reagents and solvents were used throughout the preparation and characterization.

3.2 Synthesis of 3-benzoyl-6-chloro-2-(4-chlorophenyl)chroman-4-one [3-I(a)]

A mixture of 1-(5-chloro-2-hydroxyphenyl)-3-phenylpropane-1,3-dione [2-I] (0.01 mol, 2.75 g) and 4-chlorobenzaldehyde (0.012 mol, 1.69 g) was dissolved in absolute ethanol (25 mL). Piperidine (0.5 mL) was added to the reaction mixture, which was then refluxed for 15–20 min. After completion of the reaction, the reaction mixture was allowed to cool and subsequently acidified with dilute hydrochloric acid. The precipitated product was filtered, washed thoroughly with water and crystallized from an ethanol–acetic acid mixture.



1-(5-chloro-2-hydroxyphenyl)-3-phenylpropane-1,3-dione (2-I)

4-chlorobenzaldehyde

3-benzoyl-6-chloro-2-(4-chlorophenyl)chroman-4-one [3-I(a)]

The synthesized compound [3-I(a)] was obtained as a light-yellow crystalline solid in 76% yield, with a melting point of 148 °C.

Compound: 3-benzoyl-6-chloro-2-(4-chlorophenyl)chroman-4-one [3-I(a)]
Appearance: Light-yellow crystalline solid
Yield: 76%
Melting point: 148 °C
Molecular formula: $C_{22}H_{14}Cl_2O_3$
Molecular mass: approximately 396.9 g mol^{-1}
Solubility: Soluble in $CHCl_3$, ethanol and acetone.

3.3 Preliminary characterization

The product was examined by thin-layer chromatography using silica gel G and benzene as the developing solvent. The solvent front travelled 2.4 cm, whereas the solute travelled 1.6 cm. Accordingly, Rf = 1.6/2.4 = 0.67. Thus, the compound showed an Rf value of 0.67 under the reported chromatographic conditions.

The compound did not produce coloration with neutral ferric chloride, consistent with the absence of a freely available phenolic hydroxyl group in the final cyclic product. The reported Shinoda test was positive, producing orange-red coloration with magnesium/hydrochloric acid. This observation was considered supportive of the flavonoid/chromanone-type framework.

3.4 Elemental analysis

The elemental analysis data are presented in Table 1.

Element	Found (%)	Calculated (%)
Carbon	66.47	66.52
Hydrogen	3.58	3.55

The experimental carbon and hydrogen values are in close agreement with the calculated values for the proposed molecular formula $C_{22}H_{14}Cl_2O_3$. The analytical data therefore provide additional support for the assigned molecular composition.

3.5 Mass spectral analysis

The mass spectrum was recorded under electron-ionization conditions. The reported principal ions were observed at m/z 396.91, 398.42, 400.61, 361.91, 291.63, 105.21 and 77.23.

m/z	Tentative assignment
396.91	Molecular ion region, M^+
398.42	M+2 isotope peak
400.61	M+4 isotope peak
361.91	Chlorine-loss fragment
291.63	Fragment associated with loss of benzoyl group
105.21	Benzoyl cation, $PhCO^+$
77.23	Phenyl cation, Ph^+

The cluster around m/z 397–400 is particularly significant because the molecule contains two chlorine atoms. Chlorine-containing organic compounds commonly exhibit characteristic isotope patterns because of the naturally occurring chlorine isotopes. The ion at m/z 105.21 was assigned to the benzoyl cation, $PhCO^+$, and was reported as the base peak. In mass spectrometry, the base peak corresponds to the ion having the greatest intensity in the spectrum. The m/z 77.23 ion is consistent with a phenyl-derived fragment.

The observed molecular-ion region, isotope pattern and characteristic fragmentation behaviour collectively support the proposed molecular composition and the presence of benzoyl and chlorinated aromatic groups.

3.6 Infrared spectral analysis

The IR spectrum was recorded using the KBr pellet method. Infrared spectroscopy is based on the interaction of infrared radiation with molecular vibrational modes, making it useful for identifying characteristic functional groups.

Frequency (cm^{-1})	Expected absorption range (cm^{-1})	Assignment
3072	3000–3100	Aromatic C–H stretching
2888	2850–2960	Aliphatic C–H stretching of sp^3 C-2/C-3
1720	1650–1730	C=O stretching of chroman-4-one carbonyl
1640	1620–1700	C=O stretching of benzoyl group
1610	1580–1620	Aromatic C=C stretching
1025	1000–1150	C–O–C stretching of cyclic ether
830	800–850	p-Cl-substituted aromatic C–H out-of-plane bending
768	690–770	Monosubstituted phenyl C–H out-of-plane bending

The absorption at 1720 cm^{-1} was assigned to the carbonyl group of the chroman-4-one ring, while the band at 1640 cm^{-1} was assigned to the benzoyl carbonyl group. The aromatic C=C stretching vibration was observed at 1610 cm^{-1}. The band at 1025 cm^{-1} was attributed to the cyclic C–O–C functionality. The absorptions at 830 and 768 cm^{-1} provided information concerning substituted aromatic rings.

The IR data therefore indicate the presence of the principal structural functionalities expected for the proposed compound, particularly the two carbonyl groups, aromatic rings and cyclic ether functionality.

3.7 ^{1}H NMR spectral analysis

The ^{1}H NMR spectrum was recorded at 300 MHz in $CDCl_3$ using TMS as the reference. NMR spectroscopy is a fundamental method for determining the chemical environment of nuclei in organic molecules and is widely used for structural characterization.

δ (ppm)	Multiplicity / J (Hz)	No. of H	Assignment
5.38	d, J = 11 Hz	1H	H-2 of chromanone ring
6.04	d, J = 11 Hz	1H	H-3 of chromanone ring
7.18–7.80	m	12H	Aromatic protons: 4-Cl-C_6H_4 (4H), benzoyl phenyl (5H) and chromanone aromatic ring (3H)

The proton resonance at δ 5.38 ppm appeared as a doublet with J = 11 Hz and was assigned to H-2 of the chromanone ring. The second doublet at δ 6.04 ppm with the same coupling constant was assigned to H-3. The relatively large vicinal coupling constant is consistent with the reported trans relationship of these two ring protons.

The multiplet between δ 7.18 and 7.80 ppm, integrating for 12 aromatic protons, corresponds to the protons of the 4-chlorophenyl substituent, benzoyl phenyl group and remaining aromatic protons of the chlorinated chromanone ring. The integration is consistent with the proposed structure.

4. Results And Discussion

The synthetic procedure provided the target compound in a satisfactory isolated yield of 76%. The light-yellow crystalline appearance and melting point of 148 °C provide useful physical characteristics for identification of the synthesized material. The TLC result, with an Rf value of 0.67, further indicates formation of a distinct product under the reported chromatographic conditions.

The elemental analysis showed close agreement between experimental and calculated carbon and hydrogen percentages. The mass spectrum provided particularly useful structural information. The molecular-ion region showed the characteristic isotope cluster expected for a

molecule containing two chlorine atoms. The observed fragments at m/z 361.91, 291.63, 105.21 and 77.23 are chemically reasonable for cleavage involving the chlorinated chromanone framework, benzoyl group and aromatic fragments.

The IR spectrum provided evidence for the principal functional groups. The bands at 1720 and 1640 cm^{-1} were associated with the two carbonyl environments in the molecule. The presence of aromatic C–H and C=C absorptions supported the extensive aromatic character of the compound, while the 1025 cm^{-1} absorption was consistent with the cyclic C–O–C functionality.

The ^1H NMR spectrum provided additional evidence for formation of the cyclic chromanone system. In particular, the two doublets at δ 5.38 and 6.04 ppm with J = 11 Hz represent the two vicinal protons of the heterocyclic ring. Their coupling relationship is consistent with the proposed substitution pattern. The aromatic multiplet integrating for 12 protons agrees with the three aromatic components present in the molecular structure.

Thus, physical, chromatographic, elemental and spectroscopic observations are mutually supportive of the proposed structure of 3-benzoyl-6-chloro-2-(4-chlorophenyl)chroman-4-one [3-I(a)].

5. Conclusion

A substituted chroman-4-one derivative, 3-benzoyl-6-chloro-2-(4-chlorophenyl)chroman-4-one [3-I(a)], was successfully synthesized by refluxing 1-(5-chloro-2-hydroxyphenyl)-3-phenylpropane-1,3-dione with 4-chlorobenzaldehyde in absolute ethanol in the presence of piperidine. The compound was isolated as a light-yellow crystalline solid in 76% yield and showed a melting point of 148 °C.

The proposed molecular formula $C_{22}H_{14}Cl_2O_3$ was supported by elemental analysis and the molecular-ion region of the mass spectrum. The chlorine isotope cluster and characteristic benzoyl-related fragments provided useful mass-spectral evidence. IR spectroscopy confirmed the presence of carbonyl, aromatic and cyclic ether functionalities. The ^1H NMR spectrum showed two characteristic doublets at δ 5.38 and 6.04 ppm with J = 11 Hz, together with the expected aromatic proton signals. Overall, the combined analytical data support the assigned structure of the synthesized chroman-4-one derivative.

The study demonstrates that systematic synthesis followed by complementary spectroscopic characterization provides an effective approach for establishing the structures of substituted oxygen-containing heterocyclic compounds. The synthesized compound may also serve as an intermediate for further structural modification and investigation of the physicochemical properties of related chromanone and pyrazoline derivatives.

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