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Synthesis and structural study on heterocyclic compounds 7-decanoyloxy-3-(4'-substitutedphenyl)-4H-1-benzopyran-4-ones: Crystal structure of 7-decanoyloxy-3-(4'-methylphenyl)-4H-1-benzopyran-4-one

Guan-Yeow Yeap^{a,*}, Wan-Sinn Yam^a, Paulina Dominiak^b, Masato M. Ito^c

^a Liquid Crystal Research Laboraotry, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
^b Department of Chemistry, Warsaw University, Al.Zwirki I Wigury, 101, 02-089, Warsaw, Poland
^c Department of Environmental Engineering for Symbiosis, Faculty of Engineering, Soka University, Hachioji, Tokyo 192-8577, Japan

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1. Introduction

ABSTRACT

Six new isoflavone-based esters, 7-decanoyloxy-3-(4'-substitutedphenyl)-4H-1-benzopyran-4-ones, derived from 1,3-benzenediol (resorcinol) and different *para* substituted phenylacetic acids have been synthesized and characterized. The molecular structures of the title compounds were elucidated with the employment of physical measurements and spectroscopic techniques (FTIR, 1D and 2D NMR). The conformation of 7-decanoyloxy-3-(4'-methylphenyl)-4H-1-benzopyran-4-one was determined by single crystal X-ray diffraction analysis of which the title compound crystallized into triclinic lattice with *P*-1 space group. Crystal structure of the title compound also revealed that the two phenyl rings of the central moiety were planar whilst the heterocyclic ring was found to pucker slightly from the mean plane.

Isoflavones are water-soluble chemicals found in many plants. They comprise a class of often naturally occurring organic compounds related to the flavonoids [1]. Although isoflavones are not essential nutrients, their therapeutic and medicinal values in reducing the incidence of several diseases and improving other measures linked to cardiovascular risk were well documented [2,3]. Some isoflavones and isoflavone-rich foods possess anti-cancer properties, including certain types of breast and prostate cancer [4]. Another interesting feature of isoflavone derivatives is their ability to form rod-like, calamitic liquid crystals of which many of the compounds were polymorphic, exhibiting wide thermomorphic ranges [5,6]. Hence, we are prompted to explore the new isoflavone derivatives which may possess significant use particularly in materials science.

In this paper, we report a new series of isoflavone derivatives, 7decanoyloxy-3-(4'-substitutedphenyl)-4H-1-benzopyran-4-ones wherein the decanoyloxy chain was attached to the central moiety via an ester linkage. This paper focuses on the conformational studies of the title compounds in respective liquid and solid states. The molecular structures and characteristics of the title compounds will also be discussed. The synthetic routes toward the formation of the intermediates and title compounds are shown in Fig. 1. The molecular structures of all title compounds were elucidated by spectroscopic techniques: fourier transformed infrared (FTIR) and high resolution nuclear magnetic resonance, NMR (¹H and ¹³C, homonuclear ¹H–¹H COSY, heteronuclear ¹H–¹³C HMQC and ¹H and ¹³C HMBC correlation studies). A crystal structure of 7-decanoyloxy-4'-methyl-isoflavone is further confirmed by single crystal X-ray diffraction analysis.

2. Experimental

Resorcinol (Aldrich), methanesulfonyl chloride, boron trifluoride (Merck), decanoyl chloride (Acros), phenylacetic acid, and its *p*-substituted analogues (*p*-fluoro-, *p*-chloro-, *p*-bromo-, *p*-nitro-, *p*-tolyl-, and *p*-methoxyphenylacetic acids) (TCI, Japan) were used without further purification.

2.1. Syntheses of 1-(2, 4-dihydroxyphenyl)-2-(4'-substitutedphenyl)ethanones, **1–6**

A mixture containing 5 g of the appropriate 4-substituted phenylacetic acid and 1.2 equiv of resorcinol in 40 ml BF_3 · Et_2O was

^{*} Corresponding author. Fax: +60 4 6574854.

E-mail addresses: gyyeap@usm.my, gyyeap_liqcryst_usm@yahoo.com (G.-Y. Yeap).



<u>Compound</u>	<u>R</u>
13	F
14	Cl
15	Br
16	CH_3
17	OCH ₃
18	Н

Fig. 1. The reaction scheme for compounds **13–18**. Reagents and conditions: (i) BF₃·Et₂O heated at 75 °C for 4 h; (ii) N₂ atmosphere, DMF, BF₃·Et₂O heated at 55 °C for 1.5 h; MeSO₂Cl heated at 80 °C for 2 h; (c)(i)Et₃N, DCM/DMF (ii) C₉H₁₉COCl stirred for 6 h at room temperature.

Table 1 FTIR spectral data (cm^{-1}) of compounds 13–18 in solid state (embedded in KBr).

Compounds	v (C–H) _{aliphatic}	v (C=O) _{ester}	v (C=O) _{pyranone}	$\nu (=C)_{arom}$	v (C-O)
13	2959, 2916 and 2851	1754	1637	1609	-
14	2952, 2928 and 2855	1745	1647	1576	-
15	2953, 2925 and 2853	1742	1648	1570	-
16	2959, 2925 and 2852	1743	1647	1575	-
17	2952, 2924 and 2852	1763	1638	1572	1235
18	2953, 2922 and 2851	1745	1647	1572	-

Table 2

Acquisition parameters used in the NMR measurements.

Parameters ^a	Experiment									
	¹ H NMR	¹³ C NMR	2D COSY	2D HMQC	2D HMBC					
SF (MHz)	400.1	100.6	400.1	$F_1 = 100.6$ $F_2 = 400.1$	$F_1 = 100.6$ $F_2 = 400.1$					
SW (ppm)	20	250	18	$F_1 = 200$ $F_2 = 20$	$F_1 = 200$ $F_2 = 20$					
PW (μs)	8.3 (30° flip ring)	20 (90° flip ring)	8.3 (30° flip ring)	8.3 (30° flip ring)	8.3 (30° flip ring)					
AQ(s)	4.0	1.3	0.3	0.09	0.4					
D1 (S)	1.0	2.0	2.0	1.0	1.0					
NS	32	15 000	16	64	32					
TD	66 K	65 K	$F_1 = 256$ $F_2 = 2048$	$F_1 = 512$ $F_2 = 1024$	$F_1 = 512$ $F_2 = 4096$					

^a Abbreviations: F_{1} , ¹³C channel (except 2D COSY where F_1 and F_2 are ¹H channels); SF, spectrometer frequency; SW, spectral width; AQ, acquisition time; D1, relaxation delay; NS, number of scans; TD, number of data points.

heated for 4 h at 75 $^{\circ}$ C under nitrogen atmosphere [7,8]. The mixture was cooled down to ambient temperature and poured into an ice-water bath. The oil was separated, air-dried, and recrystallized from chloroform.

1: Yield 65%. Melting point (m.p.) 140.0–141.0 °C. Analysis: calculated for $C_{14}H_{11}FO_3$. C 68.29, H 4.50%; found C 68.10%, H 4.48%. IR (KBr)/cm⁻¹: 3419 (OH), 2907 (CH₂ aliphatic), 1636 (C=O), 1598 (C=C).

 Table 3

 ¹H-¹H correlations as inferred from 2D COSY experiment for compound 14.

	1 1
Atom ^a	'H-'H COSY correlations
H2	-
H5	H6
H6	H5 and H8
H8	H6
H2' or H6'	H3' or H5'
H3'or H5'	H2' or H6'
H10	H11
H11	H10, H12 to H17
(H12 to H17) ^b	H11 and H18
H18	H12 to H17

^a Based on the atomic numbering scheme in Fig. 1.

^b The H12 to H17 atoms correlate with the methylene proton, H11 and methyl proton, H18 but their chemical shifts could not be determined due to indistinguishable ¹H chemical shifts of H12 to H17.

2: Yield 63%. m.p. 150.0–150.5 °C. Analysis: calculated for $C_{14}H_{11}ClO_3$. C 64.01, H 4.22%; found C 64.02, H 4.23%. IR (KBr)/ cm⁻¹: 3358 (OH), 2920 (CH₂ aliphatic), 1630 (C=O), 1596 (C=C).

3: Yield 68%. m.p. 170.0–170.5 °C. Analysis: calculated for $C_{14}H_{11}$ BrO₃. C 57.75, H 3.61%; found C 57.65, H 3.60%. IR (KBr)/ cm⁻¹: 3322 (OH), 2892 (CH₂ aliphatic), 1626 (C=O), 1587 (C=C).

4: Yield 69%. m.p. 144.0–145.0 °C. Analysis: calculated for $C_{15}H_{14}O_3$. C 74.36%, H 5.82%; found C 74.16, H 5.80%. IR (KBr)/ cm⁻¹: 3145 (OH), 2922, 2870 (CH₂ aliphatic), 1623 (C=O), 1584 (C=C).

5: Yield 60%. m.p. 156.0–157.0 °C. Analysis: calculated for $C_{15}H_{14}O_4$. C 69.76, H 5.46%; found C 69.50, H 5.43%. IR (KBr)/ cm⁻¹: 3412 (OH), 2836 (CH₂ aliphatic), 1631 (C=O), 1568 (C=C), 1244 (C–O).

6: Yield 63%. m.p. 138.0–139.0 °C. Analysis: calculated for $C_{14}H_{12}O_3$. C 73.07, H 5.30%; found C 73.20, H 5.32%. IR (KBr)/ cm⁻¹: 3212 (OH), 2900 (CH₂ aliphatic), 1639 (C=O), 1549 (C=C).

Table 4

¹³C-¹H correlations as inferred from the 2D HMQC and HMBC experiments for compound **14**.

Atom ^a	HMQC ¹ J	HMBC[$J(C,H)$] ² J	ЗJ	⁴ J
H2	C2	C3	C1′, C4, C8a	C2' or C6
H5	C5	-	C4, C7, C8a	C8
H6	C6	-	C4a, C8	-
H8	C8	C8a, C7	C4a, C6	C5
H2' or H6'	C2' or C6'	C1′	C4′, C3	-
H3' or H5'	C3' or C5'	C4′	C1′	-
H10 ^b	C10	C11	-	-
H11 ^b	C11	C10	-	-
H18	C18	C17	C16	-

^a Based on the atomic numbering scheme in Fig. 1.

 $^{\rm b}$ The H10 and H11 atoms correlate with the methylene carbons (C12–C15) but their J[(C, H)] values can not be determined due to indistinguishable chemical shifts of C12–C15 atoms.

2.2. Syntheses of 7-hydroxy-3-(4'-substitutedphenyl)-4H-1benzopyran-4-ones, 7-12

Five grams of 1-(2,4-dihydroxyphenyl)-2-(4-substitutedphenyl)ethanones in dry dimethylformamide (DMF) was carefully treated with 4.0 equiv of BF₃.Et₂O under nitrogen atmosphere. To this mixture, 3.0 equiv of MeSO₂Cl was added at 55 °C and stirred for 1 h. The mixture was then heated for 2 h at 80 °C [7,8] prior to being poured with rapid stirring into an ice-water bath. The product thus obtained was subsequently purified with chloroform via recrystallization.

7: Yield 59%. m.p. 202.0–203.0 °C. Analysis: calculated for C15H9 FO3. C 70.31, H 3.54%; found C 70.42, H 3.55%. IR (KBr)/ cm⁻¹: 3193 (OH), 1641 (C=O), 1598 (C=C).



Fig. 2. ¹H-¹H COSY spectrum of compound 14.



Table 5
H NMR chemical shifts (ppm) of compounds 13–18 in CDCl ₃ , where <i>m</i> = number of carbon atoms in both terminal chains. TMS was used as an internal standard.

Compounds	Chemio	cal shifts ((ppm)									
	H2	H5	H8	H2′,6′	H3′,5′	H6	H10	H11	H12-H17	H18	Ar-OCH ₃	Ar-CH ₃
13	7.99	8.32	7.12	7.31	7.11-	7.18 ^a	2.59-2.63	1.74-1.82	1.29-1.45	0.87-0.91	-	-
14	8.01	8.32	7.31	7.56	7.45	7.16-7.19	2.59-2.64	1.74-1.82	1.29-1.45	0.87-0.91	-	-
15	8.00	8.31	7.30	7.50	7.41	7.15-7.18	2.59-2.63	1.69-1.79	1.29-1.44	0.87-0.91	-	-
16	8.01	8.35	7.31	7.48	7.28	7.16-7.19	2.61-2.65	1.76-1.84	1.23-1.49	0.89-0.93	-	2.42
17	7.98	8.32	7.29	7.50	6.98	7.14-7.17	2.59-2.63	1.74-1.80	1.29-1.45	0.87-0.91	3.84	-
18	8.01	8.33	7.30	7.56	7.39-	7.74 ^a	2.59-2.63	1.74-1.80	1.29-1.45	0.87-0.91	-	-

^a Overlapped signals of H3',5' and H6.

Table 6¹³ C NMR chemical shifts (ppm) of compounds 13–18 in CDCl₃. TMS was used as an internal standard.

Compounds	Chemical	shifts (ppm)									
	C2	C3	C4	C4a	C5	C6	C7	C8	C8a	C1′	C2′,6′	C3′,5′
13	153.50	124.93	175.73	120.14	128.20	115.55	155.17	111.35	157.06	130.41	130.61	129.15
14	153.36	120.09	175.58	117.88	122.97	111.28	155.23	111.39	157.08	128.19	130.88	125.01
15	153.50	124.93	175.53	122.53	128.20	120.14	155.17	111.39	157.06	130.41	130.61	129.15
16	152.88	125.54	175.71	122.31	127.85	119.52	154.61	110.90	156.71	128.83	129.26	128.62
17	154.58	122.24	175.81	119.48	123.84	114.04	156.68	110.88	159.74	127.81	130.13	125.18
18	143.15	125.60	175.57	122.30	127.85	119.59	154.66	110.92	156.69	128.54	128.97	128.32
	C4′	C9	C10	C11	C12-C15	C16	C17	C18	Ar-CH ₃	Ar-OCH ₃		
13	134.77	171.84	34.80	24.81	23.07-29.40	32.25	22.68	14.50	-	-		
14	132.09	171.71	34.80	24.81	22.68-29.41	31.86	22.68	14.40	-	-		
15	134.77	171.46	34.42	24.81	22.68-29.41	31.86	22.68	14.11	-	-		
16	138.22	171.50	34.42	24.81	22.68-29.41	31.86	22.68	14.11	21.28	-		
17	152.60	171.49	34.41	24.81	22.68-29.41	31.86	22.68	14.11	-	55.35		
18	131.59	171.48	34.42	24.81	22.68-29.41	31.86	22.68	14.12	-	-		

8: Yield 60%. m.p. 229.0–230.0 °C. Analysis: calculated for C15H9 ClO3. C 66.07, H 3.33%; found C 66.00, H 3.33%. IR (KBr)/ cm⁻¹: 3197 (OH), 1642 (C=O), 1593 (C=C).

9: Yield 63%. m.p. 242.0–243.0 °C. Analysis: calculated for C15H9BrO3. C 56.81, H 2.86%; found C 56.70, H 2.83%. IR (KBr)/ cm^{-1}: 3177 (OH), 1641 (C=O), 1588 (C=C).

10: Yield 70%. m.p. 254.0–255.0 °C. Analysis: calculated for C16H12O3. C 76.18, H 4.74%; found C 76.30, H 4.75%. IR (KBr)/ cm⁻¹: 3188 (OH), 1623 (C=O), 1574 (C=C).

11: Yield 55%. m.p. 217.0–218.0 °C. Analysis: calculated for C16H12O4. C 71.64, H 4.51%; found C 71.68, H 4.52%. IR (KBr)/ cm⁻¹: 3137 (OH), 1638 (C=O), 1595 (C=C), 1246 (C–O).

12: Yield 61%. 199.5–200.0 °C. Analysis: calculated for C15H10O3. C 75.62, H 4.23%; found C 75.80, H 4.30%. IR (KBr)/ cm⁻¹: 3200 (OH), 1622 (C=O), 1584 (C=C).

2.3. Syntheses of 7-decanoyloxy-3-(4'-substitutedphenyl)-4H-1benzopyran-4-ones, **13–18**

Decanoyl chloride (1.2 equiv) was added to a mixture of 0.3 g of 7-hydroxy-3-(4-substitutedphenyl)-4H-1benzopyran-4-ones in DMF/CH₂Cl₂ and 0.2 ml triethylamine. The mixture was stirred at room temperature for 6 h. The solvent was later removed and diethylether was added to the residue. Triethylammonium chloride was filtered off and the product was purified through recrystallisation from absolute ethanol.

2.4. FTIR measurements

The FTIR data were recorded using a Perkin Elmer 2000-FTIR spectrophotometer in the frequency range $4000-400 \text{ cm}^{-1}$ with samples prepared in KBr discs (Table 1).

2.5. NMR measurements

NMR data were obtained using Bruker 300 MHz and 400 MHz ultrashield spectrometer. Standard Bruker pulse programs [9] were used throughout the entire experiment. The spectroscopic details of NMR are summarized in Table 2. Deuterated chloroform (CDCl₃) and dimethylsulphoxide (DMSO- d_6) were used as solvent and TMS

as internal standard. Reported chemicals shifts for isoflavone, the ¹H and ¹³C correlation spectral data were used to assign the chemical shifts of the synthesized compounds [10–12]. Complete ¹H and ¹³C NMR assignments of compounds **13–18** were obtained and substantiated with the aids of DEPT and two-dimentional ¹H–¹H correlation spectroscopy (COSY), ¹³C–¹H heteronuclear multiple quantum correlation (HMQC) and ¹³C–¹H heteronuclear multiple bond correlation (HMBC).

2.6. X-ray data collection, structure solution and refinement for compound **16**

The measurement of diffractional data was performed on a Kuma KM4CCD κ -axis diffractometer with graphite-monochromated MoK_{α} radiation and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The crystal was positioned at 62 mm from the KM4CCD camera. 2400 frames were measured at 0.5° intervals (ω scan) with a counting time of 10 s. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Oxford Diffraction Ltd. suit of programs.

The structure was solved by direct methods [13] and refined using SHELXL [14]. The refinement was based on F^2 for all reflections except those with very negative F^2 . Weighted *R* factors w*R* and all goodness-of-fit *S* values are based on F^2 . Conventional *R* factors are based on *F* with *F* set to zero for negative F^2 . The $F_o^2 > 2\sigma(-F_o^2)$ criterion was used only for calculating *R* factors and is not relevant to the choice of reflections for the refinement. The *R* factors based on F^2 are about twice as large as those based on *F*. Scattering factors were taken from crystallographic Tables 6.1.1.4 and 4.2.4.2 [15]. All hydrogen atoms were located from a difference Fourier maps. The CH₃ hydrogens were treated as part of idealized CH₃ groups with $U_{iso} = 1.5U_{eq}$, while the remainder of the hydrogen atoms were refined with the "riding" model with $U_{iso} = 1.2U_{eq}$.



3. Results and discussion

3.1. IR spectroscopy

The FTIR spectra of compounds **1–6** show the absorption bands assignable to the stretching of OH at $3137-3419 \text{ cm}^{-1}$. Bands appearing within the frequency range of 2836–2922 cm⁻¹ can be ascribed to the stretching of aliphatic C–H. Whilst the stretching of C=O (ketone) appears at 1623–1639 cm⁻¹, the signal ascribed to the C=C aromatic is observed at 1549–1598 cm⁻¹. An additional band attributable to the stretching of C-O is observed for compound **5** at 1244 cm⁻¹. Two of the earlier mentioned bands corresponding with the stretching of C-H and C=O (ketone) are absent in compounds **7–12**. Instead, the stretching of C=O (benzopyranone) at 1630–1647 cm^{-1} is recorded. Compounds **13–18**, on the other hand, show bands at 2851-2959, 1742-1763, 1637-1648, and 1609–1570 cm⁻¹, which can be assigned to the stretching of aliphatic C–H, C=O ester and C=O benzopyranone, respectively. An absorption occurring at 1235 cm⁻¹ can be attributed to the stretching of C-O in compound 17.

3.2. NMR spectroscopy

Based on a representative compound **14**, a complete assignment for the title compounds can be described. The ¹H NMR spectrum of compound **14** indicates a singlet which is attributable to H2 atom at δ = 8.00 ppm. This substantiates the occurrence of a cyclization reaction. A triplet at δ = 0.87–0.91 ppm can be assigned to methyl protons, H18 of the terminal alkyl chain. The presence of the H10 protons can be substantiated by a triplet at δ = 2.59–2.63 ppm. The other methylene protons, H11 and H12 to H17 are confirmed by the occurrence of two sets of multiplets at δ = 1.69–1.79 ppm and 1.29–1.44 ppm, respectively.

The correlations of ${}^{1}\text{H}{-}{}^{1}\text{H}$ from COSY experiment (Table 3) are employed to assign the aromatic protons. According to Fig. 2, the three sets of doublets observed at $\delta = 8.31$, 7.50 and 7.41 ppm can be ascribed to H5 and H2' (or H6') and H3' (or H5') respectively. A double doublet at $\delta = 7.15-7.18$ ppm is assigned to H6 based on the homonuclear coupling with the nearest proton (H5). The chemical shift of the H8 atom is observed as a doublet at $\delta = 7.30$ ppm.

The structure of compound **14** is further substantiated by the ¹³C NMR, HMQC and HMBC spectroscopic data (Table 4). According to the HMQC spectrum (Fig. 3), the C2 atom at δ = 153.50 ppm is assigned based on its correlation with H2 atom. Other aromatic carbons are assigned based on the correlations between C5 and H5 at δ = 128.20 ppm, C6 and H6 at δ = 120.14 ppm, C8 and H8 at δ = 111.39 ppm, C2' (or C6') and H2' (or H6') at δ = 130.61 ppm as well as C3' (or 5') and H3' (or H5') at δ = 129.15 ppm (Table 5).

The HMQC spectrum also reveals that methylene carbons, C10 atom at δ = 34.42 correlates with H10 atom (δ = 2.59–2.63) and C11 atom at δ = 24.81 correlates with H11 atom (δ = 1.69–1.79). A multiplet at δ = 1.29–1.44 ppm attributable to H12 to H17 are found to correlate to C12 to C17 atoms within δ = 31.86–22.68 ppm. The methyl carbon atom, C18 are unambiguously assigned at δ = 14.11 ppm based on its correlations with H18 atom (Table 6).



Fig. 5. The molecular structure with atom-numbering scheme of compound 16 (diamond view).



Fig. 6. The molecular packing of compound 16 (diamond view).

HMBC experiment is used to assign quaternary carbons of compound **14** (Fig. 4). The C3 atom is assigned based on its long range correlation with H2 atom at δ = 124.93 ppm. The long range HMBC cross peaks of C4 atom with H5 proton at δ = 175.53 ppm, C4a atom and H5 atom at δ = 122.53 ppm, as well as C8a atom with H8 atom at δ = 157.06 ppm confirm the positions of these atoms. The assignment of C6 atom at δ = 120.14 ppm is based on its correlation with H5 atom. The ¹³C signal of the C7 atom at δ = 155.17 ppm is confirmed via its correlation with H8 atom. The spectrum reveals cross peaks of H3' (or H5') atom with C4' atom at δ = 134.77 ppm and H3' (or H5') with C1' at δ = 130.41 ppm.

Compounds **13**, **15 16**, **17** and **18** show similar NMR spectra characteristics as discussed for compound **14** The ¹H NMR spectra for both compounds **16** and **17** each show an additional singlet at $\delta = 2.42$ and 3.84 ppm, respectively, confirmed the presence of methyl protons, Ar–CH₃ for compound **16** and methoxy protons, Ar–OCH₃ for compound **17**. The cross peaks of both protons with their respective carbons in ¹³C NMR spectra reveals the chemical shifts of methyl carbon, Ar–CH₃ at $\delta = 21.28$ ppm and methoxy carbon, Ar–OCH₃ at $\delta = 55.35$ ppm.

The results as inferred from the IR and NMR spectral data of all compounds are found to conform to those reported in the literature [6] and are consistent with the proposed structure as shown in Fig. 1.

3.3. Crystal structure analysis for compound 16

The molecular structure with the atom-numbering scheme and packing of compound are shown in Figs. 5 and 6, respectively. Crystal data of compound are collated in Table 7. The atomic coordinates, B_{iso}/B_{eq} and anisotropic displacement parameters are given in Tables 8 and 9, respectively. Tables 10 and 11 show the selected bond lengths and angles as well as the torsion angles, respectively, for compound **16**.

From Fig. 5, it is apparent that the discrete molecule of compound **16** comprise of two phenyl rings and a heterocyclic ring

Table	7
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Crystal data and	l refinement o	of compound i	16.
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Crystal data	Values
Empirical formula	$C_{26}H_{30}O_4$
Formula weight	406.50
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Dimensions	a = 5.8905(3)Å
	b = 11.2662(5)Å
	c = 16.7581(7)Å
	$\alpha = 91.909(3)^{\circ}$
	$\beta = 94.435(4)^{\circ}$
	$\gamma = 100.622(4)^{\circ}$
Volume	1088.51(9) A ³
Ζ	2
Calculated density	1.240 mgm^{-3}
Absorption coefficient	0.082 mm^{-1}
F(0 0 0)	436
Crystal size	0.35 x 0.26 x 0.18 mm
Theta range for data collection	2.99 to 27.50 deg.
Limiting indices	$-7 \leqslant h \leqslant 7$, $-14 \leqslant k \leqslant 14$, $-21 \leqslant l \leqslant 21$
Reflections collected/unique	19900/4991 [R(int) = 0.0193]
Completeness to theta = 27.50	99.4%
Max. and min. transmission	0.9853 and 0.9718
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4991/0/273
Goodness-of-fit on F ²	1.067
Final R indices [I > 2sigma(I)]	$R_1 = 0.0359$, w $R_2 = 0.1020$
R indices (all data)	$R_1 = 0.0493$, w $R_2 = 0.1051$
Largest diff. peak and hole	0.280 and -0.232 e/Å ⁻³

in the central moiety with a decanoyloxy chain attached to C7 via an ester linkage. Rings A, (C4–C5–C6–C7–C8–C9) and C, (O1–C1–C2–C3–C4–C9) are almost planar with a dihedral angle of 3.67°. The heterocyclic ring B, (C10–C11–C12–C13–C14–C15), on the other hand, is twisted from the mean plane of ring C by

Table 8	
Atomic coordinates and B_{iso}/B_{eq} of compound 16	

Aom	x	у	Z	$U_{(eq)}$
0(1)	8299(1)	7091(1)	4200(1)	19(1)
O(2)	3078(1)	7467(1)	5611(1)	21(1)
O(3)	3747(1)	3458(1)	2923(1)	21(1)
O(4)	7233(2)	3720(1)	2400(1)	43(1)
C(1)	8537(2)	7993(1)	4771(1)	18(1)
C(2)	6916(2)	8175(1)	5263(1)	15(1)
C(3)	4648(2)	7372(1)	5180(1)	16(1)
C(4)	4392(2)	6410(1)	4547(1)	16(1)
C(5)	2340(2)	5559(1)	4386(1)	19(1)
C(6)	2176(2)	4614(1)	3832(1)	20(1)
C(7)	4107(2)	4503(1)	3417(1)	18(1)
C(8)	6136(2)	5347(1)	3530(1)	19(1)
C(9)	6226(2)	6285(1)	4098(1)	16(1)
C(10)	7493(2)	9189(1)	5878(1)	15(1)
C(11)	9626(2)	9402(1)	6337(1)	18(1)
C(12)	10214(2)	10391(1)	6880(1)	21(1)
C(13)	8719(2)	11194(1)	6987(1)	20(1)
C(14)	6580(2)	10964(1)	6537(1)	18(1)
C(15)	5959(2)	9979(1)	5996(1)	17(1)
C(16)	5416(2)	3098(1)	2496(1)	22(1)
C(17)	4575(2)	1823(1)	2174(1)	22(1)
C(18)	6297(2)	1355(1)	1677(1)	22(1)
C(19)	5439(2)	45(1)	1367(1)	22(1)
C(20)	7175(2)	-442(1)	880(1)	23(1)
C(21)	6361(2)	-1749(1)	567(1)	24(1)
C(22)	8065(2)	-2205(1)	50(1)	24(1)
C(23)	7250(2)	-3494(1)	-302(1)	26(1)
C(24)	8918(2)	-3896(1)	-857(1)	30(1)
C(25)	8083(3)	-5162(1)	-1236(1)	41(1)
C(26)	9371(2)	12282(1)	7564(1)	28(1)

Table 9	
Anistropic displacement parameters ($Å^2 \times 10^3$) of compound 16 .	

Atom	U_{11}	U ₂₂	U ₃₃	U ₂₃	U ₁₃	<i>U</i> ₁₂
O(1)	18(1)	17(1)	22(1)	-7(1)	6(1)	0(1)
0(2)	19(1)	21(1)	24(1)	-3(1)	7(1)	5(1)
0(3)	22(1)	17(1)	24(1)	-7(1)	2(1)	3(1)
0(4)	42(1)	31(1)	52(1)	-20(1)	26(1)	-9(1)
C(1)	18(1)	14(1)	20(1)	-3(1)	1(1)	2(1)
C(2)	17(1)	13(1)	16(1)	0(1)	0(1)	5(1)
C(3)	18(1)	15(1)	17(1)	2(1)	3(1)	7(1)
C(4)	17(1)	14(1)	16(1)	1(1)	1(1)	5(1)
C(5)	17(1)	18(1)	23(1)	1(1)	5(1)	5(1)
C(6)	18(1)	17(1)	23(1)	-1(1)	-1(1)	2(1)
C(7)	24(1)	15(1)	15(1)	-3(1)	-1(1)	7(1)
C(8)	19(1)	19(1)	19(1)	-1(1)	5(1)	5(1)
C(9)	17(1)	15(1)	17(1)	0(1)	1(1)	3(1)
C(10)	18(1)	14(1)	14(1)	0(1)	3(1)	3(1)
C(11)	18(1)	18(1)	20(1)	0(1)	4(1)	5(1)
C(12)	19(1)	23(1)	18(1)	-2(1)	-1(1)	1(1)
C(13)	27(1)	17(1)	16(1)	-1(1)	5(1)	2(1)
C(14)	24(1)	15(1)	18(1)	0(1)	6(1)	7(1)
C(15)	19(1)	18(1)	16(1)	2(1)	2(1)	5(1)
C(16)	27(1)	21(1)	18(1)	-4(1)	5(1)	5(1)
C(17)	29(1)	17(1)	20(1)	-4(1)	3(1)	2(1)
C(18)	28(1)	18(1)	20(1)	-3(1)	4(1)	3(1)
C(19)	28(1)	17(1)	20(1)	-4(1)	2(1)	4(1)
C(20)	31(1)	18(1)	21(1)	-3(1)	5(1)	4(1)
C(21)	30(1)	19(1)	22(1)	-5(1)	4(1)	4(1)
C(22)	31(1)	20(1)	23(1)	-4(1)	5(1)	5(1)
C(23)	33(1)	19(1)	26(1)	-4(1)	6(1)	6(1)
C(24)	40(1)	23(1)	28(1)	-4(1)	7(1)	10(1)
C(25)	63(1)	26(1)	36(1)	-8(1)	12(1)	13(1)
C(26)	36(1)	22(1)	25(1)	-7(1)	3(1)	2(1)

Table 10

 \mathbf{A} lengths $(\mathbf{\hat{A}})$ and angles $(\mathbf{\hat{O}})$ of some out \mathbf{A} Colootod In

Table	11
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Torsion angle	s (°) of	compound	16.
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Selected bolid lengths (A) and angles () of compound 10.		Torsion angles () or compound To.	
C(7)-(8)	1.3791(14)	C(9)-O(1)-C(1)-C(2)	0.59(15)
C(8)-C(9)	1.3893(14)	O(1)-C(1)-C(2)-C(3)	95(16)
C(1)-O(1)-C(9)	118.18(8)	O(1)-C(1)-C(2)-C(10)	177.98(9)
C(16)-O(3)-C(7)	124.20(8)	C(1)-C(2)-C(3)-O(2)	179.21(10)
C(2)-C(1)-O(1)	125.74(9)	C(10)-C(2)-C(3)-O(2)	-0.71(15)
C(1)-C(2)C(3)	119.40(9)	C(1)-C(2)-C(3)-C(4)	0.56(14)
C(1)-C(2)-C(10)	118.77(9)	C(10)-C(2)-C(3)-C(4)	-179.37(9)
C(3)-C(2)-C(10)	121.83(9)	O(2)-C(3)-C(4)-C(9)	-176.63(9)
O(2)-C(3)-C(2)	123.55(9)	C(2)-C(3)-C(4)-C(9)	2.05(14)
O(2)-C(3)-C(4)	122.06(9)	O(2)-C(3)-C(4)-C(5)	1.10(15)
C(2)-C(3)-C(4)	114.38(8)	C(2)-C(3)-C(4)-C(5)	179.77(9)
C(9)-C(4)-C(5)	116.98(9)	C(9)-C(4)-C(5)-C(6)	2.49(15)
C(9)-C(4)-C(3)	120.91(9)	C(3)-C(4)-C(5)-C(6)	-175.32(9)
C(5) - C(4) - C(3)	122.08(9)	C(4) - C(5) - C(6) - C(7)	-0.15(16)
C(6) - C(5) - C(4)	121.56(9)	C(16) - O(3) - C(7) - C(8)	2.48(16)
C(5) - C(6) - C(7)	119.15(9)	C(16) - O(3) - C(7) - C(6)	-1/5.39(9)
C(8) - C(7) - O(3)	125.72(9) 121.45(0)	C(5) - C(6) - C(7) - C(8)	-2.61(16)
C(3) - C(7) - C(6)	121.45(9)	C(3) - C(7) - C(3)	173.30(9)
C(3) - C(3) - C(0)	117 36(9)	C(5) - C(7) - C(8) - C(9)	-174.50(5) 2 79(16)
O(1) - C(9) - C(4)	121 30(9)	C(1) = O(1) = C(3) = C(3)	2.75(10)
O(1) - C(9) - C(8)	115 28(9)	C(1) - O(1) - C(9) - C(8)	-17693(9)
C(4) - C(9) - C(8)	123 41(9)	C(5)-C(4)-C(9)-O(1)	178 64(9)
C(1) - C(10) - C(15)	118.19(9)	C(3)-C(4)-C(9)-O(1)	-3.52(15)
C(11) - C(10) - C(2)	120.54(9)	C(5)-C(4)-C(9)-C(8)	-2.29(15)
C(15)-C(10)-C(2)	121.23(9)	C(3)-C(4)-C(9)-C(8)	175.55(9)
C(12)-C(11)-C(10)	120.45(10)	C(7)-C(8)-C(9)-O(1)	178.83(9)
C(10)-C(11)	1.3979(14)	C(7)-C(8)-C(9)-C(4)	-0.29(16)
C(10)-C(15)	1.4000(14)	C(1)-C(2)-C(10)-C(11)	-44.36(14)
C(11)–C(12)	1.3899(14)	C(3)-C(2)-C(10)-C(11)	135.57(10)
C(12)-C(13)	1.3902(15)	C(1)-C(2)-C(10)-C(15)	133.61(11)
C(13)-C(14)	1.3943(15)	C(3)-C(2)-C(10)-C(15)	-46.46(14)
C(13)–C(26)	1.5080(14)	C(15)-C(10)-C(11)-C(12)	-1.59(15)
C(14) - C(15)	1.3849(14)	C(2)-C(10)-C(11)-C(12)	176.45(9)
C(16) - C(17)	1.4981(14)	C(10)-C(11)-C(12)-C(13)	0.12(16)
C(17) = C(18)	1.5164(15)	C(11) - C(12) - C(13) - C(14)	0.93(16)
C(18) - C(19)	1.5287(14)	C(11) - C(12) - C(13) - C(26)	-1/8.76(10)
C(19) - C(20)	1.5217(15) 1.5226(14)	C(12) - C(13) - C(14) - C(15) C(26) - C(12) - C(14) - C(15)	-0.49(13)
C(20) - C(21)	1.5230(14) 1.5230(14)	C(13) - C(14) - C(15) - C(10)	-1.00(16)
C(22) - C(23)	1.5250(14) 1.5254(15)	C(11) - C(10) - C(15) - C(14)	2.02(15)
C(22) = C(24)	1 5217(16)	C(2)-C(10)-C(15)-C(14)	-17600(9)
C(24) - C(25)	1.5204(16)	C(7) - O(3) - C(16) - O(4)	-12.19(17)
C(11)-C(12)-C(13)	121.58(10)	C(7)-O(3)-C(16)-C(17)	168.22(9)
C(12)-C(13)-C(14)	117.64(9)	O(4)-C(16)-C(17)-C(18)	-0.73(17)
C(12)-C(13)-C(26)	121.72(10)	O(3)-C(16)-C(17)-C(18)	178.84(9)
C(14)-C(13)-C(26)	120.64(10)	C(16)-C(17)-C(18)-C(19)	178.77(9)
C(15)-C(14)-C(13)	121.53(9)	C(17)-C(18)-C(19)-C(20)	-178.89(9)
C(14)-C(15)-C(10)	120.57(10)	C(18)-C(19)-C(20)-C(21)	179.82(9)
O(4)-C(16)-O(3)	124.32(10)	C(19)-C(20)-C(21)-C(22)	177.34(9)
O(4)-C(16)-C(17)	126.42(10)	C(20)-C(21)-C(22)-C(23)	-177.53(9)
O(3)-C(16)-C(17)	109.25(9)	C(21)-C(22)-C(23)-C(24)	176.39(10)
C(16)-C(17)-C(18)	112.95(9)	C(22)-C(23)-C(24)-C(25)	-177.89(10)
C(17)-C(18)-C(19)	112.40(9)	O(3)-C(16)-C(17)-C(18)	178.84(9)
C(20) - C(19) - C(18)	112.82(9)	C(16)-C(17)-C(18)-C(19)	178.77(9)
C(19) - C(20) - C(21)	113.79(9)	C(17) - C(18) - C(19) - C(20)	-178.89(9)
C(22) - C(21) - C(20)	113.23(9)	C(18) - C(19) - C(20) - C(21)	177.24(0)
C(21) - C(22) - C(23)	114.40(9)	C(19) - C(20) - C(21) - C(22) C(20) - C(21) - C(22) - C(22)	177 52(0)
C(2+) - C(2) - C(22)	113.10(9)	C(20) - C(21) - C(22) - C(23) C(21) - C(22) - C(23) - C(24)	-177.55(9) 176.39(10)
$(23)^{-}(24)^{-}(23)$	115./1(10)	C(21) - C(22) - C(23) - C(24)	-177 89(10)
			-1//09/101

41.07°. The methyl group, C26 and decanoyloxy chain, O3 are orientated slightly out of plane of the rings to which they are attached. The angle of O3-C6-C7 is 112.80° and that of C13-C14-C26 is 120.64°.

The bond lengths of C13-C26 (1.5080(14) Å), C2-C10 (1.4854(14) Å), and O3-C7 (1.3904(11) Å) are characteristics of single bonds. On the other hand, the C=O linkage of benzopyranone, 02-C3 (1.2337 (12)Å) and that of the ester, 04-C16 (1.1920(13) Å) are characteristics double bonds as observed in other isoflavone derivatives [16,17]. Fig. 6 also shows that the decanoyloxy chain attached to C7 via an ester linkage is linear with no folding. The torsion angle between C3–C2–C10–C15 is –46.46°. This value is the lowest in hitherto reported isoflavone system according to Shoja [18] in 1992. The then lowest value reported was -42.80°.

The packing of the molecules (Fig. 6) shows that they lie anti parallel to each other. The molecules are arranged in layers and stacked along the b axis with two molecules in one unit cell. There are no anomalously short intermolecular contacts in the crystal of compound 16. The crystal cohesion resulted from dipolar interactions between anti parallel ester groups as well as van der Waals interaction of neighbouring molecules stabilize the packing of the molecules.

The molecular structure of compound 16 based on crystallography methods (Fig. 6) confirmed the structure inferred from FTIR and NMR spectroscopic techniques.

4. Supplementary material

Crystallographic data for compound 16 have been deposited at Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK and can be retreated upon request. Structure factors table is available from the author.

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References

- [1] P.B. Kaufman, J.A. Duke, H. Brielmann, J. Boik, J.E. Hoyt, J. Altern. Complement. Med. 3 (1) (1997) 7.
- A. Crisafulli, D. Altavilla, H. Marini, Menopause 12 (2005) 186. [2]
- S.Y. Cheng, N.S. Shaw, K.S. Tsai, J. Womens Health (Larchmt) 13 (2005) 1080. [3] [4] R.A. Dixon, Annu. Rev. Plant. Biol. 55 (2004) 225.
- [5] T. Hirose, K. Tsuya, T. Nikigaki, E. Idaka, S. yano, J. Liq. Cryst. 4 (1989) 653. [6] G.Y. Yeap, W.S. Yam, M.M. Ito, Y. Takahashi, Y. Nakamura, W.A.K. Mahmood, P.L. Boey, S.A. Hamid, E. Gorecka, J. Liq. Cryst. 34 (2007) 649.
- [7] A. Pelter, R.S. Ward, T.I. Gray, Chem .Soc. Perkin I (1976) 2475.
- [8] A. Pelter, R.S. Ward, R.I. Bass, Chem. Soc. Perkin Trans. I (1978) 666.
- [9] Bruker program 1D WIN-NMR (release 6.0) and 2D WIN-NMR (release 6.1).
- [10] A. Pelter, R.S. Ward, J. Chem. Soc. Perkin Trans. I (1978) 666.
- [11] H.C. Jha, F. Zilliken, Can. J. Chem. 58 (1980) 1211.
- [12] K. Wahala, T.A. Hase, J. Chem. Soc. Perkin Trans. I (1991) 3005.
- [13] G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467.
 [14] G.M. Sheldrick, SHELXL93: Program for the Refinement of Crystal Structures, University of Göttingen, Germany,
- [15] A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer, Dordrecht, 1992.
- [16] M. Kaneda, Y. Iitaka, S. Shibata, Acta Cryst. B29 (1973) 2827.
- [17] T.P. Lewis, K. Wahala, A. Hoikkala, I. Mutikainen, H.M. Qing, H. Adlercreutz, J. Tikkanen, Tetrahedron 56 (2000) 7805.
- [18] M. Shoja, Acta Cryst. C48 (1992) 2033.