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

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ABSTRACT

Six new isoflavone-based esters, 7-decanoyloxy-3-(4′-substitutedphenyl)-4*H*-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)-4*H*-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.

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1. Introduction

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, 7-decanoyloxy-3-(4′-substitutedphenyl)-4*H*-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 (^{1}H and ^{13}C, homonuclear ^{1}H–^{1}H COSY, heteronuclear ^{1}H–^{13}C HMQC and ^{1}H and ^{13}C 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 $BF_3{\cdot}Et_2O$ was

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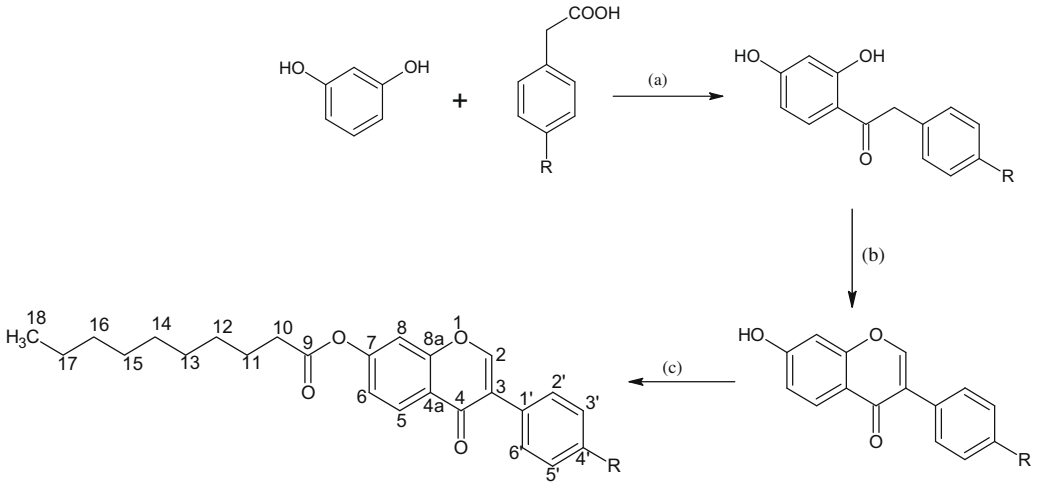

Compound	R
13	F
14	Cl
15	Br
16	CH_3
17	OCH_3
18	H

Fig. 1. The reaction scheme for compounds **13–18**. Reagents and conditions: (i) $BF_3{\cdot}Et_2O$ heated at 75 °C for 4 h; (ii) N_2 atmosphere, DMF, $BF_3{\cdot}Et_2O$ heated at 55 °C for 1.5 h; $MeSO_2Cl$ heated at 80 °C for 2 h; (c)(i)Et_3N, DCM/DMF (ii) $C_9H_{19}COCl$ 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	ν (C–H)$_{aliphatic}$	ν (C=O)$_{ester}$	ν (C=O)$_{pyranone}$	ν (=C)$_{arom}$	ν (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, ^{13}C channel (except 2D COSY where F_1 and F_2 are ^{1}H 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 °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 (CH_2 aliphatic), 1636 (C=O), 1598 (C=C).

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