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6-Methyl-3-phenylthiochroman-4-one and 6-Methoxy-3-phenylthiochroman-4-one: Configurational Preference of the Phenylthio Group at the Third Position due to Remote Substitution

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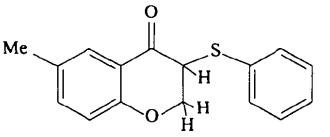
(*Received 2 September 1996; accepted 4 March 1997*)

Abstract

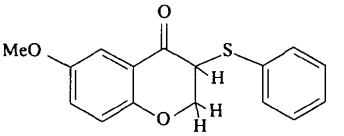
The pyran ring adopts a distorted sofa conformation in the title compounds, 6-methyl-3-phenylthiochroman-4-one ($C_{16}H_{14}O_2S$), (I), and 6-methoxy-3-phenylthiochroman-4-one ($C_{16}H_{14}O_3S$), (II). The S atom substituted at the third position is attached equatorially in (II) and axially in (I). High-resolution proton NMR studies could not provide a conclusive explanation for this feature.

Comment

Isoflavanoids, the compounds based on a 3-phenylchroman skeleton, belong to the family Papilionoidae of the Leguminosae of the plant kingdom. They exhibit a large number of structural variations (Dewick, 1988). The title compounds, (I) and (II), belong to the series of 3-phenylchromanones, synthesized by our group, with S as the bridge between the phenyl ring and the C atom at the third position of the heterocycle of the chroman ring system. The bond lengths in the pyran ring (involving atoms O1, C2, C3, C4, C9 and C9′) are normal with negligible variations in their values in both compounds. The bond angles around C4 differ significantly from the ideal sp^2 values. Similarly, the bond angles around C9 deviate from the ideal 120°. The bond angle C3—S—C10 in (I) is 3.4° lower than in (II).



(I)



(II)

The dihedral angles between the planes of the phenyl rings C5–C9 and C10–C15 are 31.9 (4) and 67.1 (9)° in (I) and (II), respectively. In both compounds, the pyran ring adopts a distorted sofa conformation, with C2 deviating from the mean plane formed by the other atoms of this ring [0.651 for (I) and 0.663 Å for (II)], the normal conformation of the pyran ring being half chair (Alex *et al.*, 1993). As seen from the torsion angle O2—C4—C3—S, the S atom is axially connected to the C3 atom in (I) whereas it is connected equatorially in (II). The crystal structures are stabilized by intermolecular van der Waals interactions, although compound (II), which has a relatively higher density, is marked by tighter packing. However, the only difference between the two compounds is the substitution of a methyl group at a remote site (C5) in (I) instead of a methoxy group in (II).

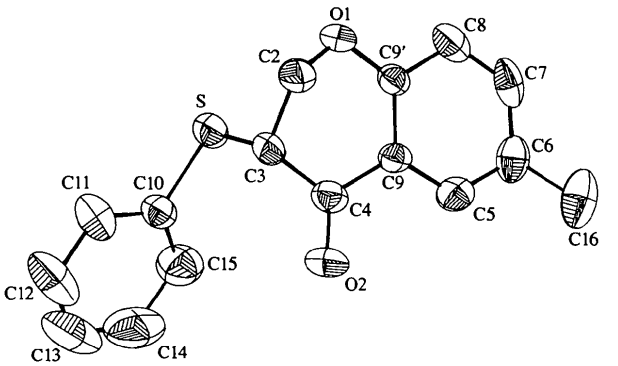


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the molecular structure and atom-numbering scheme of (I). The displacement ellipsoids are drawn at the 50% probability level.

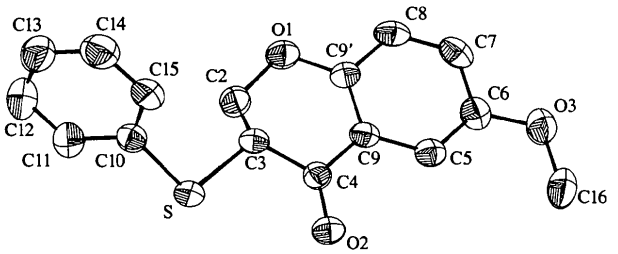


Fig. 2. *ORTEP*II (Johnson, 1976) plot of the molecular structure and atom-numbering scheme of (II). The displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compounds were prepared from their respective bromo derivatives, 6*R*-3-bromochroman-4-one [*R* = methyl in (I) and methoxy in (II)], which were prepared by the reaction of the respective chroman-4-ones with Br in chloroform or diethyl ether at room temperature. Thiophenol (1.2 mmol) was added to a solution of triethylamine (1.5 mmol) in methanol (15 ml) and this mixture was stirred for 5 min. The respective 3-bromochroman-4-one was added in portions over a period of 10 min. The mixture was stirred at room temperature for 45 min, poured into ice-cold water and extracted with diethyl ether. The organic layer was washed with 2*N* hydrochloric acid and then with water to obtain a 90–95% yield of the 3-phenylthiochroman-4-ones (Santhosh, 1994). The details of the proton NMR data of the two compounds are as follows; compound (I): ^{1}H NMR [400 MHz, $CDCl_3$, δ (p.p.m.)]: 2.26 (*s*, 3H, Ar-CH_3), 3.96 (*dd*, 1H, $J_{c,b}$ = 2.32, $J_{c,a}$ = 4.62 Hz, H_c), 4.68 (*dd*, 1H, $J_{c,a}$ = 4.62, $J_{a,b}$ = 13.87 Hz, H_a), 5.23 (*dd*, 1H, $J_{b,c}$ = 2.32, $J_{b,a}$ = 13.87 Hz, H_b), 6.8–7.9 (*m*, 8H, Ar-H); compound (II): ^{1}H NMR [400 MHz, $CDCl_3$, δ (p.p.m.)]: 3.77 (*s*, 3H, $ArOCH_3$), 4.10 (*dd*, 1H, $J_{c,b}$ = 2.70, $J_{c,a}$ = 5.40 Hz, H_c), 4.49 (*dd*, 1H, $J_{c,a}$ = 5.42, $J_{a,b}$ = 11.35 Hz, H_a), 4.58 (*dd*, 1H, $J_{b,c}$ = 2.72, $J_{b,a}$ = 11.35 Hz, H_b), 6.9–7.5 (*m*, 8H, Ar-H). With respect to the differences in the orientation of the H atom substituting at C3, no conclusions could be drawn from the small differences obtained in the δ values of the proton peaks [3.96 for (I) and 4.1 for (II)].

Compound (I)

Crystal data

$C_{16}H_{14}O_2S$
M_r = 270.33
Monoclinic
$P2_1/c$
a = 9.278 (5) Å
b = 9.826 (4) Å
c = 15.237 (10) Å
β = 93.24 (10)°
V = 1386.9 (13) Å^3
Z = 4
D_x = 1.295 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8–12°
μ = 0.228 mm^{-1}
T = 293 (2) K
Prismatic
0.44 × 0.33 × 0.31 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2061 measured reflections
1909 independent reflections
1631 reflections with $I > 2\sigma(I)$

R_{int} = 0.041
θ_{max} = 24.98°
h = 0 → 11
k = −5 → 11
l = −18 → 18
2 standard reflections
frequency: 60 min
intensity decay: 3.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.131
S = 1.080
1909 reflections
228 parameters
H-atom coordinate parameters refined only

$w = 1/[\sigma^2(F_o^2) + (0.0822P)^2 + 0.3283P]$
$(\Delta/\sigma)_{max}$ = −0.001
$\Delta\rho_{max}$ = 0.249 e Å^{-3}
$\Delta\rho_{min}$ = −0.223 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

S—C10	1.766 (10)	C3—C4	1.497 (6)
S—C3	1.833 (7)	C3—C2	1.509 (8)
O1—C9′	1.363 (5)	C9—C4	1.477 (6)
O1—C2	1.434 (7)		
C10—S—C3	102.7 (3)	O1—C9′—C8	117.5 (4)
C9′—O1—C2	114.0 (4)	O1—C9′—C9	122.6 (2)
C4—C3—C2	110.4 (3)	C9′—C9—C4	119.9 (4)
C4—C3—S	107.6 (4)	O2—C4—C9	122.9 (4)
C2—C3—S	108.2 (3)	O2—C4—C3	122.0 (3)
O1—C2—C3	110.9 (5)	C9—C4—C3	115.1 (4)
C9′—O1—C2—C3	−54.5 (4)	C2—C3—C4—O2	152.4 (3)
C4—C3—C2—O1	57.8 (4)	S—C3—C4—O2	−89.6 (3)
S—C3—C2—O1	−59.8 (4)	C2—C3—C4—C9	−30.3 (4)
C2—O1—C9′—C9	22.9 (4)	S—C3—C4—C9	87.6 (3)
O1—C9′—C9—C4	5.2 (4)	C3—S—C10—C11	86.6 (5)
C9′—C9—C4—C3	−0.1 (4)	C3—S—C10—C15	−98.7 (5)

Compound (II)

Crystal data

$C_{16}H_{14}O_3S$
M_r = 286.33

Mo $K\alpha$ radiation
λ = 0.71073 Å

Monoclinic
$P2_1/c$
a = 13.113 (4) Å
b = 15.260 (6) Å
c = 6.762 (5) Å
β = 92.36 (4)°
V = 1352.0 (12) Å^3
Z = 4
D_x = 1.407 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 8–12°
μ = 0.243 mm^{-1}
T = 293 (2) K
Prismatic
0.38 × 0.35 × 0.18 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2274 measured reflections
2088 independent reflections
1749 reflections with $I > 2\sigma(I)$

R_{int} = 0.018
θ_{max} = 25.00°
$h = -15 \rightarrow 15$
$k = -18 \rightarrow 0$
$l = 0 \rightarrow 8$
2 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.131
S = 1.058
2088 reflections
237 parameters
H-atom coordinate parameters refined only

$w = 1/[\sigma^2(F_o^2) + (0.0823P)^2 + 0.3635P]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.329 e Å^{-3}
$\Delta\rho_{min}$ = −0.280 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (II)*

S—C10	1.783 (3)	C3—C2	1.513 (4)
S—C3	1.811 (3)	C3—C4	1.516 (4)
O1—C9′	1.367 (3)	C9—C4	1.478 (3)
O1—C2	1.429 (3)		
C10—S—C3	99.3 (1)	O1—C9′—C8	116.8 (2)
C9′—O1—C2	114.3 (2)	O1—C9′—C9	123.1 (2)
C2—C3—C4	108.0 (2)	C9′—C9—C4	120.4 (2)
C2—C3—S	111.8 (2)	O2—C4—C9	124.2 (2)
C4—C3—S	112.7 (2)	O2—C4—C3	123.5 (2)
O1—C2—C3	110.6 (2)	C9—C4—C3	112.2 (2)
C9′—O1—C2—C3	50.7 (3)	C2—C3—C4—O2	−141.2 (3)
C4—C3—C2—O1	−64.8 (3)	S—C3—C4—O2	−17.2 (4)
S—C3—C2—O1	170.8 (2)	C2—C3—C4—C9	42.2 (3)
C2—O1—C9′—C9	−14.4 (4)	S—C3—C4—C9	166.1 (2)
O1—C9′—C9—C4	−7.3 (4)	C3—S—C10—C15	−54.1 (3)
C9′—C9—C4—C3	−8.7 (3)	C3—S—C10—C11	128.1 (3)

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

The authors wish to thank the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, India, for data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1051). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1075–1077

β-1-*N*-Acetamido-D-glucopyranose

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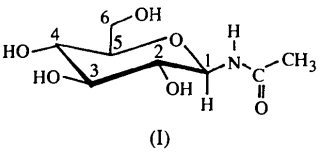
(*Received 13 November 1996; accepted 4 March 1997*)

Abstract

In the title molecule, $C_8H_{15}NO_6$, the pyranose ring adopts the usual $^4C_1(D)$ conformation and the *N*-acetyl group exists in the *Z–anti* conformation. The orientation of the primary alcohol group is *gauche*.

Comment

The glycan (oligosaccharide) components of glycoproteins are known to play vital roles in protein folding, protein targeting and cellular recognition (Cumming, 1992; Imperiali & Rickert, 1994). Elucidation of the structural basis of their biological roles represents a fundamental and challenging problem in glycobiological research (Dwek, 1996). A systematic study initiated recently by the present authors is focused on the structural aspects of *N*-glycoproteins. The title compound, (I), was chosen for the current X-ray crystallographic investigation as it represents the simplest model of the linkage region (2-deoxy-2-acetamido-β-D-glucopyranosylasparagine, GlcNAcβAsn).



(I)