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Three Novel Isomeric Pyranocoumarins from *Calophyllum teysmannii*: Calanone, Isocalanone and Teysmanone A[†]

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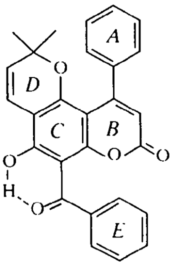
Abstract

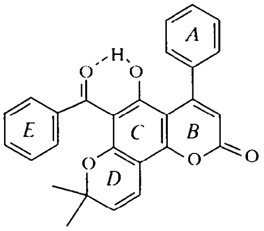
The crystal and molecular structures of the three title compounds, calanone [6-benzoyl-5-hydroxy-2,2-dimethyl-10-phenyl-2*H*,8*H*-benzo[1,2-*b*:3,4-*b*′]dipyran-8-one, (I)], isocalanone [6-benzoyl-5-hydroxy-8,8-dimethyl-4-phenyl-2*H*,8*H*-benzo[1,2-*b*:3,4-*b*′]dipyran-2-one, (II)] and teysmanone A [10-benzoyl-5-hydroxy-8,8-dimethyl-4-phenyl-2*H*,8*H*-benzo[1,2-*b*:5,4-*b*′]coumarin, (III)], all having formula $C_{27}H_{20}O_5$ but different isomeric structures, are reported. All of the compounds have the basic coumarin structure. Strong intramolecular hydrogen bonding is present between the carbonyl and hydroxyl groups in (I) and (II), but medium strong intermolecular hydrogen bonding is present in (III). The nature of the hydrogen bonding determines the planarity of the PhC=O groups. Structures (I) and (II) have a similar PhC=O conformation dictated by intramolecular O—H···O=C hydrogen bonding, in which the carbonyl groups are twisted away from the phenyl ring. The C(*E-ortho*)—C(*E*)—C=O torsion angle is 32.8 (2)° in (I) and −40.8 (2)° in (II). In the absence of intramolecular hydrogen bonding, the C=O group is nearly in plane with the benzene ring in (III) with a C(*E-ortho*)—C(*E*)—C=O torsion angle of −2.7 (3)°.

Comment

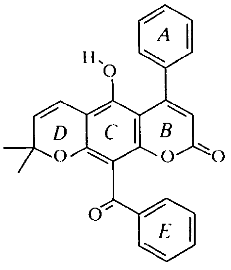
Plants of the *Calophyllum* genus (Guttiferae) are well known for their rich source of oxygen heterocyclic secondary metabolites such as coumarins and xanthones. Following the discovery that the coumarin calanonide A, isolated from the tropical rainforest tree *Calophyllum lanigerum* var. *austrocoriaceum* (Kashman *et al.*, 1992), represents a novel subclass of HIV-1 specific reverse transcriptase inhibitors (Boyer *et al.*, 1993), much attention has been focused on the study of these plants (Fuller *et al.*, 1994; McKee *et al.*, 1995, 1996; Pengparp *et al.*, 1996; Galinis *et al.*, 1996). Recently, Boyd and coworkers isolated a unique benzoyl-substituted coumarin, calanone, from the latex of *Calophyllum teysmannii* var. *inophylloide* and established its structure as (I) by spectroscopic methods (Gustafson *et al.*, 1994). We have also examined the bark of *C. teysmannii* and isolated three isomeric coumarins, namely, calanone, (I), isocalanone, (II), and teysmanone A, (III), and established their structures by spectroscopic methods. Recently, we were able to obtain suitable crystals of the three coumarins for single-crystal X-ray analysis which confirmed the structures assigned earlier by spectroscopic methods. This paper reports the crystal structures of these three unique isomeric highly substituted pyranocoumarins.



(I)



(II)



(III)

The basic fragment containing rings *A*, *B* and *C* is common to all three compounds. Rings *D* and *E* are attached in different ways to produce (I), (II) and (III) as shown above. The interplanar angles between rings *A* and *B* are 68.31 (6) and 69.00 (6)° in (I) and (II), respectively, but 57.47 (7)° in (III). The interplanar angles between the rings *B* and *C* are 2.17 (8), 4.50 (7) and 2.0 (1)° in (I), (II) and (III), respectively. The carbonyl groups are not in the plane of the phenyl ring *E* in (I) and (II). The C(*E-ortho*)—C(*E*)—C=O torsion angles are 32.8 (2) and −40.8 (2)° in (I) and (II), respectively. However, the C(*C-ortho*)—C(*C*)—C=O torsion angles are 19.9 (2) and −19.4 (2)°, for (I) and (II), respectively. This is attributed to the strong intramolecular hydrogen bonding between the C=O and O—H groups. Phenyl ring *E* and the carbonyl group are found to be close to planarity [−2.7 (3)°] in the absence of such intramolecular bonding in (III). However, a medium strong intermolecular hydrogen

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[†] Systematic names: 6-benzoyl-5-hydroxy-2,2-dimethyl-10-phenyl-2*H*-pyrano[2,3-*f*]coumarin, 6-benzoyl-5-hydroxy-8,8-dimethyl-4-phenyl-8*H*-pyrano[2,3-*h*]coumarin and 10-benzoyl-5-hydroxy-8,8-dimethyl-4-phenyl-8*H*-pyrano[3,2-*g*]coumarin.

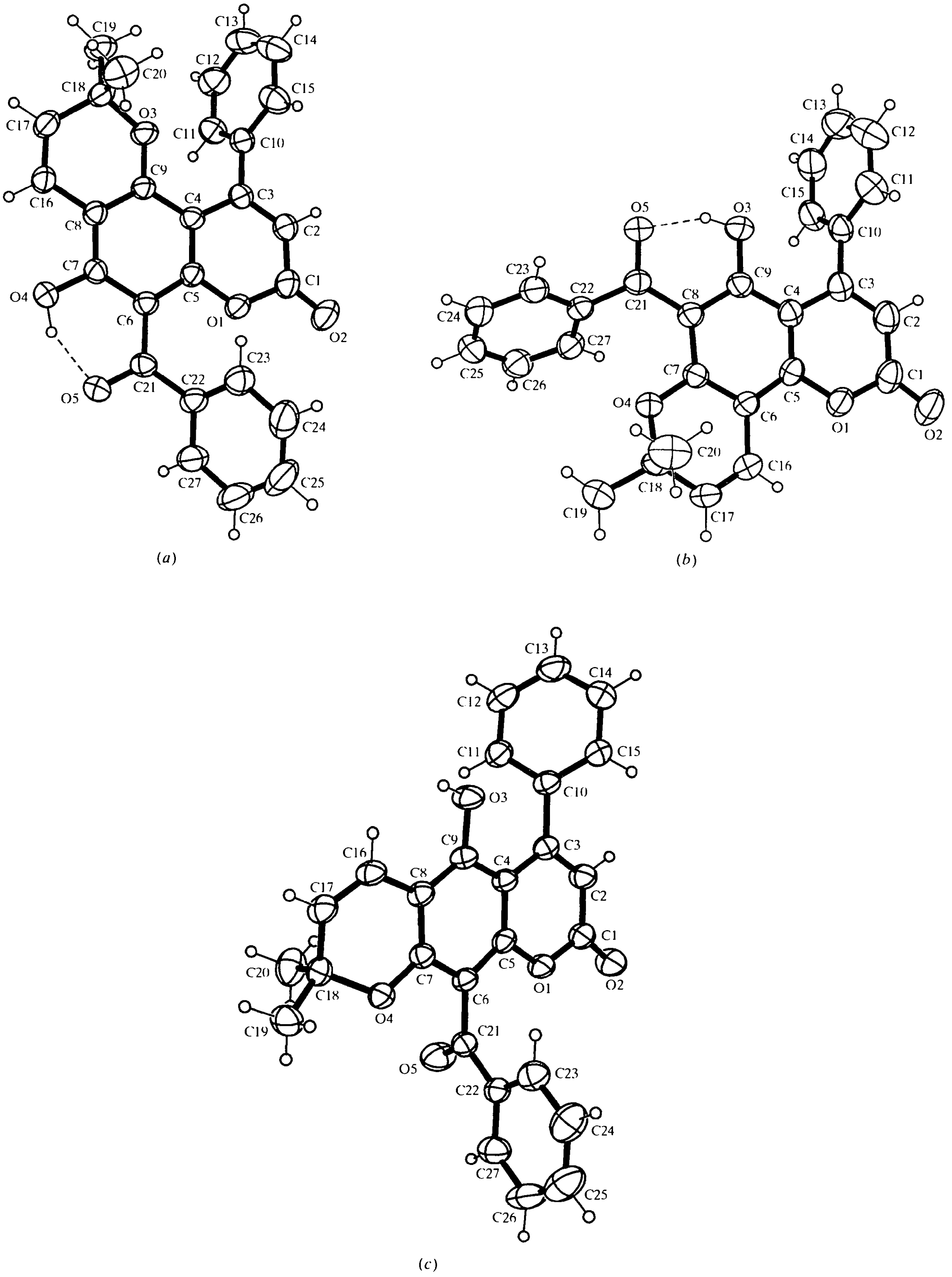

Fig. 1. A view showing the labelling of the non-H atoms for (*a*) (I), (*b*) (II) and (*c*) (III). Displacement ellipsoids are shown at 50% probability levels.

bond is present between O3—H and C1═O2 in (III). The respective O—H, H···O and O···O distances and the O—H···O angle are 0.87 (2), 1.72 (2), 2.510 (2) Å and 149 (2)° in (I), 0.92 (2), 1.65 (3), 2.511 (2) Å and 154 (2)° in (II), and 0.83 (3), 2.01 (3), 2.786 (2) Å and 156 (2)° in (III).

Experimental

The title compounds were isolated by chromatographic methods from the hexane and ethyl acetate extracts of the dried powdered bark of *C. teysmannii* as described earlier (Cao, Sim *et al.*, 1998; Cao, Chong *et al.*, 1998) and crystals were grown from ethanolic solutions.

Compound (I)

Crystal data

$C_{27}H_{20}O_5$
$M_r = 424.452$
Orthorhombic
*Fdd*2
$a = 22.7727$ (4) Å
$b = 38.3529$ (7) Å
$c = 9.6310$ (2) Å
$V = 8411.7$ (3) Å^3
$Z = 16$
$D_x = 1.341$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 2.08$–$27.01°$
$\mu = 0.092$ mm^{-1}
$T = 297$ (2) K
Cut large rock
$0.38 \times 0.32 \times 0.28$ mm
Yellow

Data collection

Siemens SMART CCD diffractometer
Frames and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.715$, $T_{\max} = 0.977$
11 465 measured reflections

4141 independent reflections
3757 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 27.91°$
$h = -29 \rightarrow 14$
$k = -49 \rightarrow 49$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.084$
$S = 1.036$
4141 reflections
294 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 4.7806P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.147$ e Å^{-3}
$\Delta\rho_{\min} = -0.129$ e Å^{-3}

Extinction correction: *SHELXTL* (Siemens, 1996*a*)
Extinction coefficient: 0.00154 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.5 (8)

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

O1—C5	1.372 (2)	C7—O4	1.340 (2)
O1—C1	1.401 (2)	C7—C8	1.404 (2)
O2—C1	1.197 (2)	C8—C9	1.384 (2)
C1—C2	1.442 (3)	C8—C16	1.463 (2)
C2—C3	1.352 (2)	C9—O3	1.348 (2)
C3—C4	1.452 (2)	C16—C17	1.323 (2)
C3—C10	1.501 (2)	C17—C18	1.493 (3)
C4—C5	1.403 (2)	C18—O3	1.480 (2)
C4—C9	1.429 (2)	C18—C20	1.514 (3)
C5—C6	1.409 (2)	C18—C19	1.522 (2)
C6—C7	1.424 (2)	O5—C21	1.240 (2)
C6—C21	1.484 (2)	C21—C22	1.487 (2)
C5—O1—C1	123.12 (13)	C8—C7—C6	121.58 (15)
O2—C1—O1	116.6 (2)	C9—C8—C7	119.13 (14)
O2—C1—C2	128.0 (2)	C9—C8—C16	118.27 (14)
O1—C1—C2	115.42 (15)	C7—C8—C16	122.50 (15)
C3—C2—C1	122.7 (2)	O3—C9—C8	120.81 (13)
C2—C3—C4	119.26 (15)	O3—C9—C4	116.95 (14)
C2—C3—C10	118.3 (2)	C17—C16—C8	119.6 (2)
C4—C3—C10	122.41 (14)	C16—C17—C18	122.0 (2)
C5—C4—C9	116.10 (14)	O3—C18—C17	109.99 (13)
C5—C4—C3	118.46 (14)	O3—C18—C20	107.4 (2)
C9—C4—C3	125.42 (14)	C17—C18—C20	111.4 (2)
O1—C5—C4	119.89 (14)	O3—C18—C19	103.49 (14)
O1—C5—C6	115.99 (13)	C17—C18—C19	112.3 (2)
C4—C5—C6	124.09 (14)	C20—C18—C19	111.9 (2)
C5—C6—C7	116.30 (13)	C9—O3—C18	120.22 (13)
C5—C6—C21	125.99 (14)	O5—C21—C6	118.35 (15)
C7—C6—C21	117.70 (15)	O5—C21—C22	117.08 (14)
O4—C7—C8	116.11 (14)	C6—C21—C22	124.48 (15)
O4—C7—C6	122.28 (14)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H1···O5	0.87 (2)	1.72 (2)	2.510 (2)	149 (2)

Compound (II)

Crystal data

$C_{27}H_{20}O_5$
$M_r = 424.452$
Monoclinic
$P2_1/n$
$a = 6.0017$ (3) Å
$b = 27.3003$ (13) Å
$c = 12.8273$ (6) Å
$\beta = 95.303$ (1)°
$V = 2092.7$ (2) Å^3
$Z = 4$
$D_x = 1.347$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5944 reflections
$\theta = 1.76$–$29.36°$
$\mu = 0.093$ mm^{-1}
$T = 293$ (2) K
Cut long needle
$0.30 \times 0.20 \times 0.15$ mm
Yellow

Data collection

Siemens SMART CCD diffractometer
Frames and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.785$, $T_{\max} = 0.982$
12 794 measured reflections

5131 independent reflections
3487 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 29.36°$
$h = -8 \rightarrow 7$
$k = -36 \rightarrow 37$
$l = -17 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.120$
$S = 1.053$
5131 reflections
294 parameters
H atoms: see below

$\Delta\rho_{\max} = 0.224$ e Å^{-3}
$\Delta\rho_{\min} = -0.176$ e Å^{-3}
Extinction correction: *SHELXTL* (Siemens, 1996*a*)
Extinction coefficient: 0.0117 (11)

$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2$
$+ 0.3604P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

O1—C5	1.373 (2)	C7—O4	1.347 (2)
O1—C1	1.387 (2)	C7—C8	1.424 (2)
O2—C1	1.208 (2)	C8—C9	1.420 (2)
C1—C2	1.432 (2)	C8 · · C21	1.472 (2)
C2—C3	1.347 (2)	C9—O3	1.341 (2)
C3—C4	1.458 (2)	C16—C17	1.320 (2)
C3—C10	1.494 (2)	C17—C18	1.491 (2)
C4—C5	1.398 (2)	C18—O4	1.484 (2)
C4—C9	1.416 (2)	C18—C19	1.511 (2)
C5—C6	1.391 (2)	C18—C20	1.519 (2)
C6—C7	1.390 (2)	O5—C21	1.246 (2)
C6—C16	1.458 (2)	C21—C22	1.488 (2)
C5—O1—C1	122.03 (13)	C6—C7—C8	121.53 (13)
O2—C1—O1	115.7 (2)	C9—C8—C7	117.61 (13)
O2—C1—C2	127.8 (2)	C9—C8—C21	118.57 (12)
O1—C1—C2	116.56 (14)	C7—C8—C21	123.73 (13)
C3—C2—C1	123.3 (2)	O3—C9—C4	117.68 (13)
C2—C3—C4	118.49 (14)	O3—C9—C8	120.27 (14)
C2—C3—C10	118.97 (14)	C4—C9—C8	122.04 (13)
C4—C3—C10	122.51 (14)	C17—C16—C6	119.6 (2)
C5—C4—C9	115.92 (13)	C16—C17—C18	121.47 (14)
C5—C4—C3	118.10 (14)	O4—C18—C17	109.58 (12)
C9—C4—C3	125.88 (14)	O4—C18—C19	104.69 (12)
O1—C5—C6	114.31 (13)	C17—C18—C19	112.48 (13)
O1—C5—C4	121.01 (13)	O4—C18—C20	107.58 (12)
C6—C5—C4	124.65 (14)	C17—C18—C20	110.86 (14)
C7—C6—C5	117.84 (13)	C19—C18—C20	111.3 (2)
C7—C6—C16	118.28 (13)	C7—O4—C18	119.02 (11)
C5—C6—C16	123.87 (14)	O5—C21—C8	120.07 (13)
O4—C7—C6	120.12 (12)	O5—C21—C22	116.58 (13)
O4—C7—C8	118.35 (13)	C8—C21—C22	123.26 (12)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H· · ·*A*	*D*—H	H· · ·*A*	*D*· · ·*A*	*D*—H· · ·*A*
O3—H1· · ·O5	0.92 (2)	1.65 (2)	2.511 (2)	154 (2)

Compound (III)

Crystal data

$C_{27}H_{20}O_5$
$M_r = 424.452$
Monoclinic
$P2_1/c$
$a = 9.0418$ (5) Å
$b = 16.7577$ (10) Å
$c = 14.1879$ (9) Å
$\beta = 106.315$ (1)°
$V = 2063.2$ (2) Å^3
$Z = 4$
$D_x = 1.366$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 1.93$–29.27°
$\mu = 0.094$ mm^{-1}
$T = 296$ (2) K
Cut long thin needle
0.30 × 0.20 × 0.13 mm
Light yellow

Data collection

Siemens SMART CCD diffractometer
Frames and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.784$, $T_{\max} = 0.988$
12 285 measured reflections

5047 independent reflections
3475 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 29.27°$
$h = -12 \rightarrow 11$
$k = -21 \rightarrow 22$
$l = -13 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.128$
$S = 1.057$
5047 reflections
294 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0430P)^2$
$+ 0.7114P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.222$ e Å^{-3}
$\Delta\rho_{\min} = -0.181$ e Å^{-3}
Extinction correction: *SHELXTL* (Siemens, 1996*a*)
Extinction coefficient: 0.0024 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 5. *Selected geometric parameters (Å, °) for (III)*

O1—C1	1.369 (2)	C7—O4	1.360 (2)
O1—C5	1.379 (2)	C7—C8	1.406 (2)
O2—C1	1.217 (2)	C8—C9	1.394 (2)
C1—C2	1.426 (2)	C8—C16	1.460 (2)
C2—C3	1.358 (2)	C9—O3	1.353 (2)
C3—C4	1.452 (2)	C16—C17	1.327 (3)
C3—C10	1.494 (2)	C17—C18	1.501 (2)
C4—C5	1.403 (2)	C18—O4	1.471 (2)
C4—C9	1.423 (2)	C18—C20	1.512 (3)
C5—C6	1.385 (2)	C18—C19	1.518 (3)
C6—C7	1.385 (2)	O5—C21	1.208 (2)
C6—C21	1.512 (2)		
C1—O1—C5	121.87 (13)	C6—C7—C8	122.2 (2)
O2—C1—O1	116.4 (2)	C9—C8—C7	118.65 (15)
O2—C1—C2	126.5 (2)	C9—C8—C16	124.7 (2)
O1—C1—C2	117.06 (15)	C7—C8—C16	116.7 (2)
C3—C2—C1	123.3 (2)	O3—C9—C8	122.09 (15)
C2—C3—C4	118.5 (2)	O3—C9—C4	116.60 (15)
C2—C3—C10	115.7 (2)	C8—C9—C4	121.31 (15)
C4—C3—C10	125.54 (14)	C17—C16—C8	119.9 (2)
C5—C4—C9	116.04 (15)	C16—C17—C18	121.5 (2)
C5—C4—C3	117.43 (14)	O4—C18—C17	109.19 (14)
C9—C4—C3	126.52 (15)	O4—C18—C20	107.28 (15)
O1—C5—C6	114.18 (14)	C17—C18—C20	111.9 (2)
O1—C5—C4	121.49 (15)	O4—C18—C19	104.65 (15)
C6—C5—C4	124.30 (15)	C17—C18—C19	111.5 (2)
C5—C6—C7	117.16 (15)	C20—C18—C19	112.0 (2)
C5—C6—C21	121.24 (15)	C7—O4—C18	116.77 (13)
C7—C6—C21	121.3 (2)	O5—C21—C22	121.9 (2)
O4—C7—C6	116.96 (15)	O5—C21—C6	119.1 (2)
O4—C7—C8	120.77 (15)		

Table 6. *Hydrogen-bonding geometry (Å, °) for (III)*

D—H· · ·*A*	*D*—H	H· · ·*A*	*D*· · ·*A*	*D*—H· · ·*A*
O3—H1· · ·O2^{i}	0.83 (3)	2.01 (3)	2.786 (2)	156 (2)

Symmetry code: (i) $1 + x, y, z$.

Preliminary cell constants were obtained from 45 frames (width 0.3° in ω). Final cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. A frame width of 0.3° in ω and a counting time of 20 s per frame at a crystal-to-detector distance of 5.0 cm were used. The collected frames were integrated using the preliminary orientation matrix. The structures were solved by direct methods. All the H atoms could be located in difference Fourier maps. The positional and isotropic displacement parameters of the hydroxy H atoms were refined in the least-squares cycles for all three compounds. Riding models were used to place the rest of the H atoms.

For all compounds, data collection: *SMART* (Siemens, 1996*b*); cell refinement: *SAINT* (Siemens, 1996*b*); data reduction: *SAINT*; program(s) used to solve structures: *SHELXS*86

(Sheldrick, 1990); program(s) used to refine structures: *SHELXTL* (Siemens, 1996*a*); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Financial support for this research and the award of a research scholarship to SGC from the National University of Singapore are gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1085). Services for accessing these data are described at the back of the journal.

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Thiosemicarbazid-1-ium Dihydrogenphosphate

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Abstract

Thiosemicarbazid-1-ium dihydrogenphosphate, $CH_6N_3S^+.H_2PO_4^-$, unlike the semicarbazide complex compounds, does not exhibit temperature-dependent ferroelectric properties. X-ray structure determination at room temperature has shown that the crystal is centrosymmetric (space group $C2/c$) and thermal mobility of the structural units is relatively low. This allowed the refinement of all H-atom parameters without any space constraints. The $H_2PO_4^-$ anions, with a distorted tetrahedral configuration, are hydrogen bonded to the thiosemicarbazidium cations. The average observed $U_{\rm iso}$ value for the H atoms (0.045 Å^2) suggests that the protons are well fixed at their sites, and the extensive three-dimensional system of moderately short hydrogen bonds forms a structure in which dynamic disorder by hydrogen 'jumping' is not pronounced.

Comment

Different complexes of semicarbazide with, for example, copper(II) and zinc chlorides (Nardelli *et al.*, 1963), and the salts with hydrobromide (Boldrini, 1971), hydrochloride (Nardelli *et al.*, 1965) and nitric acid (Wawrzak *et al.*, 1981), have attracted considerable attention due to their interesting physical properties connected with ferroelectric phase transitions. In this family of compounds, the phase transitions are related to the high molecular polarizability of inorganic and organic sublattices. In particular, it is interesting to study the role of inorganic anions in orienting the organic unit in a way which promotes a non-centrosymmetric molecular arrangement (Datta *et al.*, 1994; Herbert, 1978). Certain characteristics of the phase transitions in these compounds are also connected with the dynamics of the protons in the hydrogen bonds, which in the present structure can be formed easily between the N···O and O···O atoms. In our search for ferroelectric materials, a new compound of thiosemicarbazide with phosphoric acid, thiosemicarbazid-1-ium dihydrogenphosphate (TSCDHP), has been synthesized. Measurement of the dielectric constant and thermal analysis by differential scanning calorimetry did not indicate, however, any temperature-

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