Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1178). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 1:1 Deoxycholic Acid–Salicylic Acid Complex

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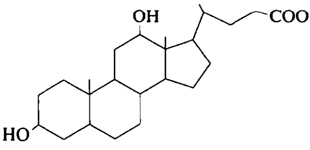
Abstract

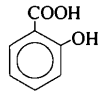
The 1:1 complex of deoxycholic acid [(3α,5β,12α)-3,12-dihydroxy-5-cholan-24-oic acid, $C_{24}H_{40}O_4$; DCA] and salicylic acid ($C_7H_6O_3$; SA) has been determined. The side-chain conformation of deoxycholic acid is *trans*, which is coupled with an intermediate conformation of ring *D*. No characteristic bilayer structure was found. Salicylic acid is trapped in a channel formed by DCA molecules.

Comment

Deoxycholic acid (DCA) is one of the bile acids having the interesting property of forming channel-type complexes with a wide variety of chemical compounds, for example, aliphatic and aromatic hydrocarbons, fatty acids, *etc.* (Giglio, 1984, and references therein). Many X-ray crystallographic studies have been carried out. Up to now, DCA–guest complexes have been grouped into three crystal systems, namely, orthorhombic, tetragonal and hexagonal. The first system is commonly observed and is able to include large non-polar molecules, while the rest can only accommodate small polar molecules such as ethanol and water (Coiro, Andrea & Giglio, 1979; Candeloro De Sanctis, Giglio, Petri & Quagliata, 1979). In this study, the crystal structure of DCA–SA (1/1) has been determined.



DCA



SA

The molecular structure is shown in Fig. 1. The DCA molecule is composed of four rings, *A*, *B*, *C* and *D*. Rings *A* and *B* are arranged in a *cis* manner resulting in the arched shape of the molecule. Rings *A*, *B* and *C* are considered to be rigid, whereas ring *D* is flexible and related to the conformation of the side chain. This feature varies among the DCA–guest complexes, although the side chain exhibits a '*gauche*' conformation and ring *D* approaches a 'half-chair' conformation in orthorhombic crystals (Giglio, 1984). The conformations in the present crystal are different. The conformation of ring *D* is suitably described by Δ, the phase angle of pseudo-rotation, and φ_m, the maximum angle of torsion (Altona, Geise & Romers, 1968). Selected torsion angles of the side chain are given in Table 1. The value of Δ in the DCA–SA complex is 14.5°. This value causes ring *D* to adopt a conformation intermediate between half chair and envelope. Five torsion angles of ring *D*, *i.e.* C17—C14—C15—C19, C18—C17—C14—C15, C19—C18—C17—C14, C15—C19—C18—C17

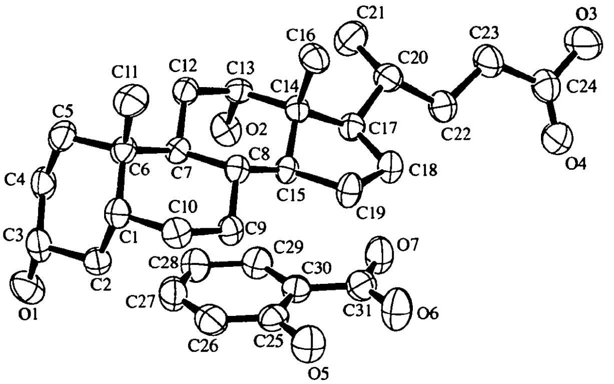


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the DCA–SA complex. Ellipsoids are drawn at the 50% probability level, while isotropic H-atom displacement parameters are represented by spheres of arbitrary size.

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and C14—C15—C19—C18, are in good agreement with postulated values of 46.3, −41.0, 20.1, 8.5 and −33.9, respectively (Altona, Geise & Romers, 1968). The torsion angle C17—C20—C22—C23 of −169.4 (3)° indicates a '*trans*' conformation. This value correlates well with the value calculated from a van der Waals energy map (Giglio & Quagliata, 1975). In orthorhombic crystals of the DCA–ferrocene complex (Miki, Kasai, Tsutsumi, Miyata & Takemoto, 1987), Δ and the torsion angle C17—C20—C22—C23 have values of 5.5 and 66.8°, respectively, which indicate a 'half-chair' conformation of ring *D* and a '*gauche*' conformation of the side chain.

The bond lengths and angles of salicylic acid agree well with published values (Sundaralingam & Jensen, 1965), except for the angles H43—O7—C31 [117.9 (3)°] and H44—O5—C25 [112.3 (3)°]. This implies some interaction between DCA and the salicylic acid molecule. The packing in the orthorhombic DCA–guest crystal is bilayer. Rows of DCA molecules are developed along **b** and rows are linked by hydrogen bonding involving the O4 and O3 atoms of two adjacent molecules (Giglio, 1984). In the case of the DCA–SA complex, this type of hydrogen bonding is not formed. The hydrophobic and hydrophilic layers are not clearly seen, as shown in Fig. 2. Salicylic acid molecules lie along the *a* axis and are trapped in the channel formed by DCA molecules. This type of packing correlates well with the intermediate conformation of ring *D* and the *trans* conformation of the side chain (Giglio & Quagliata, 1975). Such a structure of DCA may be observed when the side chain of DCA has no hydrogen bond. Moreover, related molecules without hydrogen bonding, *e.g.* $2\beta,3\alpha$-dichloro-5α-cholestane (Geise, Romers & Rutten, 1966) and $2\alpha,3\beta$-dibromo-5α-cholestane (Geise & Romers, 1966), also show similar conformations of ring *D* and the side chain.

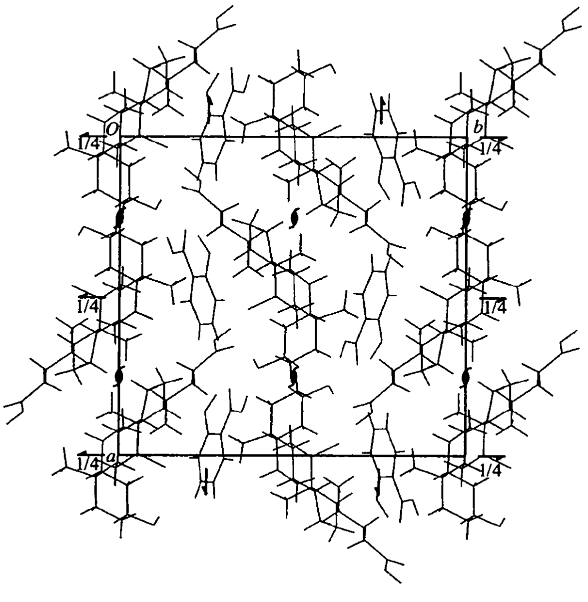

Fig. 2. The crystal packing of the DCA–SA complex viewed along the *c* axis.

Experimental

The title complex was crystallized at 298 K from an equimolar mixture of DCA and SA in ethanol solution by slow evaporation.

Crystal data

$C_7H_6O_3.C_{24}H_{40}O_4$
$M_r = 530.70$
Orthorhombic
$P2_12_12_1$
$a = 15.866\ (2)$ Å
$b = 17.320\ (2)$ Å
$c = 10.3158\ (9)$ Å
$V = 2834.8\ (5)$ Å^3
$Z = 4$
$D_x = 1.243$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 19.2$–$20.7°$
$\mu = 0.699$ mm^{-1}
$T = 296.2$ K
Prismatic
0.40 × 0.30 × 0.15 mm
Colorless

Data collection

Rigaku AFC-7*S* diffractometer
ω–2θ scans
Absorption correction: none
2963 measured reflections
2900 independent reflections
2455 reflections with $I > 1.5\sigma(I)$

$R_{\rm int}$ not measured
$\theta_{\rm max} = 67.56°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 12$
3 standard reflections every 150 reflections intensity decay: −0.68%

Refinement

Refinement on *F*
$R = 0.0413$
$wR = 0.0444$
$S = 1.867$
2455 reflections
343 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.00006|F_o|^2]$
$(\Delta/\sigma)_{\rm max} = 0.0320$

$\Delta\rho_{\rm max} = 0.12$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.10$ e Å^{-3}
Extinction correction: type 2, Gaussian isotropic
Extinction coefficient: 0.00000
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles (Å, °)*

C17—C20—C22—C23	−169.4 (3)	C15—C19—C18—C17	8.0 (4)
C17—C14—C15—C19	46.2 (3)	C19—C18—C17—C14	20.3 (3)
C14—C15—C19—C18	−33.8 (3)	C18—C17—C14—C15	−40.0 (3)

The ω-scan width was $(1.3 + 0.14\tan\theta)°$ and the scan speed was 16° min^{-1}. Refinement was by the full-matrix least-squares method.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: OA1013). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Guanidinium Hydrogen Squarate

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Abstract

The unit cell contains two crystallographically independent formula units, $CH_6N_3^+.C_4HO_4^-$, that are connected *via* a three-dimensional network of hydrogen bonds. Two crystallographically independent anion–cation chains are formed and arranged in two crystallographically independent layers and stacked along the *b* axis. The guanidine molecule accepts a proton from the squaric acid. Anions and cations are nearly planar. In the anions, the C—O and especially the C—C bond lengths differ significantly, and the C—C—C angles deviate significantly from 90°.

Comment

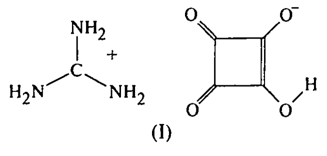
This article is part of a project investigating the nonlinear optical properties of new classes of organic compounds involving salts of guanidine derivatives, optically active amines and amino acids with 'oxocarbons' (West, 1980), *i.e.* deltic, squaric, croconic and rhodisonic acids and their sulfur derivatives. The series began with the structure of L-argininium hydrogen squarate (Angelova, Velikova, Kolev & Radomirska, 1996) followed by the structure of *R*-(−)-2-phenylglycinium hydrogen squarate (Angelova, Petrova, Radomirska & Kolev, 1996).

The structures of guanidinium hydrogen oxalate (Adams, 1978) and guanidinium nitrate (Katrusiak & Szafranski, 1994) have been investigated previously. Guanidinium nitrate has phase transitions in the crystal at 296 and 384 K. There is a paucity of structural information for guanidine compounds, even though they have been shown to be cardiovascular, antihistamine and antidiabetic drugs, as well as antibacterial and anti-inflammatory agents (Greenhill & Lue, 1993).

It has been shown that the O atom in guanidinium oxalate monohydrate can accept up to four hydrogen bonds. A search in the chemical literature showed no entry for the title compound. The structures of hydrogen squarates of $[H_2NMe_2]^+$ (Wang & Stucky, 1974), and some alkali (Bull, Ladd, Povey & Shirley, 1973; Semmingsen, 1976) and 3*d* metals such as Co and Ni (Brach, Roziere, Anselment & Peters, 1987) are already known.

The asymmetric unit of the title crystal, (I), contains two guanidinium cations and two hydrogen squarate anions. The anions and cations are nearly planar. The maximum deviations from the best planes defined by the C atom and the N atoms of the cations are 0.09 (4) (H1*B*) and 0.11 (4) Å (H5*A*), and maximum deviations from the best planes defined by the C atoms of the anions are 0.11 (4) (H2) and 0.11 (4) Å (H7). In the anions, the C—C bond lengths at the C atom carrying the OH group [mean values of 1.433 (4) and 1.437 (4) Å] are shorter than the remaining two C—C bond lengths of the ring [mean values of 1.487 (4) and 1.480 (4) Å] and C—C—C angles deviate significantly from 90° [maximum deviation of 3.0 (2)°]. The C—N bond lengths in the cations are in the range 1.318 (4)–1.332 (4) Å, the N—C—N angles in the range 119.3 (3)–121.1 (3)°, the H—N—H angles in the range 114 (4)–129 (4)° and the C—N—H angles in the range 115 (3)–126 (3)°.

A three-dimensional network of hydrogen bonds is observed in the crystal and all H atoms are involved.



(I)