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Isolation and crystal ctructure of sulfur from *Capparis spinosa* fruits

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Abstract: The purpose of this paper studied single crystal structure of S_8 isolated firstly from *Capparis spinosa* fruits. The S_8 crystal structure was investigated by single-crystal X-ray crystallographic analysis crystallizes in the monoclinic system, M=256.48. space group Fddd. Unit cell parameters a=10.456(7)Å, b=12.908(9)Å, c=24.483(17)Å, V=3305(4)Å^3, Z=16, F(000)=2048. The final R_1=0.0915, wR_2=0.1820.

Key words: *Capparis spinosal*; element sulfur; single-crystal X-ray diffraction; crystal structure

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刺山柑果实中硫单质的分离与晶体结构

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摘 要：从刺山柑果实中首次分离纯化得到 S_8 单质。经 X-射线单晶衍射分析，确认该化合物为 S_8 晶体，M=256.48。晶体属斜方晶系，空间群 Fddd。晶胞参数 a=10.456(7)Å，b=12.908(9)Å，c=24.483(17)Å，V=3305(4)Å^3，Z=16，F(000)=2048，R_1=0.0915，wR_2=0.1820。

关键词：刺山柑；硫单质；X-射线单晶衍射；晶体结构

Capparis spinosa is a vine that belongs to family Capparaceae, genus *Capparis*, mainly distributed in Xinjiang, Tibet and other places in China, lives on extremely arid Gobi desert or arid stony mountain(Liu *et al.*, 2011). As the Uyghur folk medicine, the root bark, leaf, fruit of *C. spinosa* were widely used for treatment of gout, rheumatoid arthritis (Chinese medicine dictionary, 1977). Chemical studies on *C. spinosa* have reported many beneficial chemical compounds(Ao, *et al.*, 2007). Including volatile oil, mustard oil glycoside, alkaloid, terpenes, flavonoids and other ingredients; moreover, laboratory studies have shown that the extract of the plant has pharmacological effects such as liver protection, antiinflammatory, antiviral, antioxidant, immune regulation, hypoglycemic, reduc-

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ing blood lipid and other biological activity(Chen, *et al.*, 2010; Li, *et al.*, 2007; Nizar *et al.*, 2010; Yang, *et al.*, 2008, 2010; Gagdoli C, 1999). This paper reports the single-crystal structure of S_8 isolated firstly from the fruit parts of *C. spinosa*, which will facilitate the study of this plant and lay a foundation for its exploitation and utilization.

1 Experimental

1.1 General experimental procedures

The melting point was performed on X-4 micro melting point apparatus(uncorrected). The IR spectra was recorded on a Fourier transform infrared spectrometer with KBr pellets. Single-crystal structure of S_8 was measured on an X-ray diffraction surface detector Bruker SMART CCD Ⅱ diffractometer.

1.2 Plant material

The fruit parts of *C. spinosal* were collected from South Xinjiang in July 2008. It was identified by Professor Li Zhi-Jun College of Plant Science, Tarim University.

1.3 Extraction and isolation

The air-dried and finely powdered fruit parts of *C. spinosa* were extracted with petroleum ether for three times at room temperature, every time for 48 h, then filtrated. The filtrate was evaporated under reduced pressure to gain crude petroleum ether extraction. Firstly, the extraction was separated by silica gel column chromatography, further purified by repeated silica gel column Chromatography, finally using crystallization to get a light yellow compound.

1.4 Preparation of the single crystal

The light yellow compound was recrystallized in the mixture solution of petroleum ether and ethyl acetate, and the single crystal was obtained at the constant temperature(20 ℃).

1.5 Crystallographic data colection and structure determination

A yellow single crystal with dimensions 0.34 mm ×0.27 mm×0.19 mm was put on a Bruker SMART CCD Ⅱ diffractometer equipped with a graphite-monochromatic Moka radiation (0.71073Å) by using φ-ω scan mode. Out of the total 3 813 reflections collected in the range of 2.64° to 25.09°. 739 were unique($R_{int}=0.0338$). An absorption correction by using SADABS software was applied. Atomic coordinates of atoms were dissolved with SHELXS-97 program firstly, and then atomic coordinates and anisotropic thermal parameters of all atoms were determined from difference Fourier map. The crystal structure was solved by direct methods using SHELXS-97 program. All atoms were refined by full-matrix least-squares techniques on F2 with SHELXTL-97. The final R indices($I>2\sigma(I)$)were $R_1=0.0915$, $wR_2=0.1820$. The largest peak and hole on final difference Fourier map were 1.298 and -2.367 e. $Å^{-3}$, respectively.

2 Results and Analysis

The single crystal of S_8 was recrystallized under the mixture solution of petroleum ether and ethyl acetate at the constant temperature and isolated from *C. spinosa* fruits for the first time. The composition and configuration of S_8 have been investigated by single-crystal X-ray crystallographic analysis crystallizes in the monoclinic system. The crystal data and structure refinement are given in Table 1. The atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. Bond lengths and bond angles are listed in Table 3. Anisotropic displacement parameters($Å^2\times10^3$) for title compound are listed in Table 4. Torsion angles for title compound are listed in Table 5 and Figure 1 shows the drawing of the molecule configuration and Figure 2 shows the packing diagram of the unit cell of compound. We obtained S_8 from *C. spinosa* fruits through separation and purification, but how it formed was still not clear, maybe as the report went the biochemical pathway leading to the accumulation of elemental sulphur remained unexplained(Lognay, *et al.*, 1993), maybe other reasons need to be futher investigation.

Table 1　Crystal data and structure refinement for title compound

Item	Parameter
Empirical formula	S_8
Formula weight	256.48
Temperature	296(2)K
Wavelength	0.71073Å
Crystal system, space group	Orthorhombic, Fddd
Unit cell dimensions	a=10.456(7)Å, α=90 deg b=12.908(9)Å, β=90 deg c=24.483(17)Å, γ=90 deg
Volume	3305(4) Å^3
Z, Calculated density	16, 2.062 Mg/m^3
Absorption coefficient	2.061 mm^{-1}
F(000)	2 048
Crystal size	0.34 mm×0.27 mm×0.19 mm
Theta range for data collection	2.64 to 25.09 deg
Limiting indices	−5≤h≤12, −15≤k≤15, −29≤l≤29
Reflections collected/unique	3813/739(R_{int}=0.0338)
Completeness to theta=25.09	100.0%
Absorption correction	None
Max. and Min. transmission	0.7017 and 0.5400
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	739/0/37
Goodness-of-fit on F^2	1.046
Final R indices [I>2σ(I)]	R_1=0.0915, wR_2=0.1820
R indices(all data)	R_1=0.0939, wR_2=0.1846
Largest diff. peak and hole	1.298 and −2.367 e. Å^{-3}

Table 2　Atomic coordinates(×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for title compound

Atom	x	y	z	Ueq
S(2)	341(1)	7803(1)	4238(1)	39(1)
S(3)	−428(1)	7298(1)	4959(1)	37(1)
S(4)	1056(1)	7027(1)	5486(1)	37(1)
S(1)	359(1)	6578(1)	3705(1)	36(1)

U(eq)is defined as one third of the trace of the orthogonalized Uij tensor

Table 3　Bond lengths [Å] and angles [°] for title compound

Bond lengths	Bond angles
S(2)-S(3)	2.0464(19)
S(3)-S(2)-S(1)	107.90(8)
S(2)-S(1)	2.049(2)
S(2)-S(3)-S(4)	107.45(9)
S(3)-S(4)	2.048(2)
S(4)#1-S(4)-S(3)	108.52(8)
S(4)-S(4)#1	2.046(3)
S(1)#1-S(1)-S(2)	109.15(8)
S(1)-S(1)#1	2.046(3)

Symmetry transformations used to generate equivalent atoms: #1 −x+1/4, −y+5/4

Table 4　Anisotropic displacement parameters (Å^2×10^3)for title compound

U11	U22	U33	U23	U13	U12	
S(2)	50(1)	30(1)	35(1)	9(1)	−4(1)	1(1)
S(3)	36(1)	42(1)	34(1)	−2(1)	5(1)	10(1)
S(4)	53(1)	32(1)	27(1)	−8(1)	−5(1)	3(1)
S(1)	27(1)	55(1)	27(1)	−3(1)	−6(1)	−2(1)

The anisotropic displacement factor exponent takes the form: −2 pi^2[h^2 a*^{2}U11+...+2 h k a* b* U12]

Table 5　Torsion angles [°] for title compound

S(1)-S(2)-S(3)-S(4)	100.75(8)
S(2)-S(3)-S(4)-S(4)#1	−98.84(9)
S(3)-S(2)-S(1)-S(1)#1	−97.98(9)

Symmetry transformations used to generate equivalent atoms: #1 −x+1/4, −y+5/4

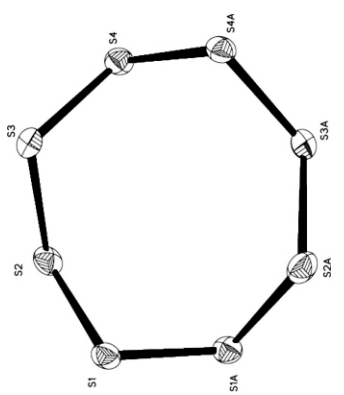

Fig. 1　The molecular structure of the title compound

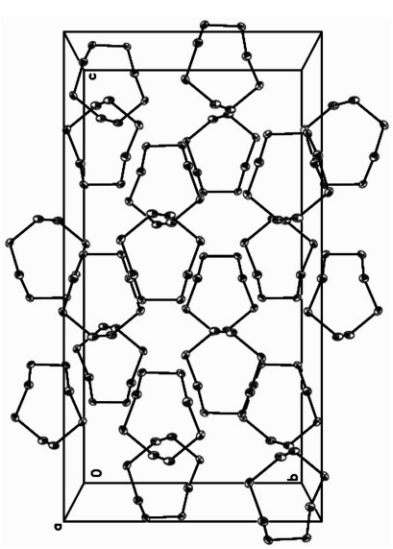

Fig. 2 Packing diagram of the unit cell of title compound

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