

# 甘草酸铵对抗坏血酸与铅配合能力的影响

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**摘要** 用pH电势法研究不同甘草酸铵浓度和不同温度时甘草酸铵对抗坏血酸与铅配合能力的影响。在生理条件下,甘草酸铵的浓度为 $5.0 \times 10^{-4} \text{ mol/L}$ 时,抗坏血酸与铅配合稳定常数为 $\lg k_1 = 8.72$ ,  $\lg k_2 = 6.91$ 。结果表明,随温度降低和甘草酸铵浓度增大,配合稳定常数增大。

**关键词** 甘草酸铵 抗坏血酸 铅 pH 电势法 配合稳定常数

甘草酸(MG)是豆科植物甘草的主要成分甘草酸的单铵盐,是1种三萜皂甙类化合物,有广泛的药理作用,抗坏血酸(VC)与铅( $\text{Pb}^{2+}$ )能形成配合物,对铅中毒的预防和治疗有重要的意义。为此,我们在体外接近生理条件下,用pH电势法研究了不同浓度的MG及不同温度对VC与 $\text{Pb}^{2+}$ 配合能力的影响。

## 1 实验方法

1.1 仪器与药品: SA-720型离子计(U.S.A); PU-8800型UV/VIS分光光度计(Philips) CS-501型超级恒温水浴(重庆试验设备厂); 抗坏血酸(济南第三制药厂), 甘草(市售); 其它试剂均为分析纯,用重蒸水配制

1.2 MG的制备及鉴定: 从甘草中提取 $\text{MG}^{[1]}$ , 得白色针状结晶, 熔点 $213 \sim 218^\circ\text{C}$ (温度计未校正),  $\text{UV}\lambda_{\text{max}} = 252 \text{ nm}$ (5% EtOH)。

1.3 VC加合质子常数的测定: 取浓度为 $5.984 \times 10^{-2} \text{ mol/L}$  VC溶液2ml, 加入 $0.5 \text{ mol/L}$  NaCl溶液20ml, 维持离子强度, 加重蒸水至50ml。在 $37^\circ\text{C}$ 恒温充分搅拌, 氮气保护下用 $1.609 \times 10^{-2} \text{ mol/L}$  NaOH溶液进行电势滴定, 记录加入NaOH溶液的体积和溶液的pH值变化。

1.4 VC- $\text{Pb}^{2+}$ 配合稳定常数测定: 在同方法1.3中未经滴定的溶液中, 加入浓度为 $8.544 \times 10^{-2} \text{ mol/L}$ 的 $\text{Pb}^{2+}$ 溶液0.5ml, 其它实验操作与1.3相同。

1.5 不同MG浓度时VC- $\text{Pb}^{2+}$ 配合稳定常数的测定: 配制浓度为 $5.342 \times 10^{-4} \text{ mol/L}$  MG溶液, 在 $37^\circ\text{C}$ , 分别加入MG溶液1、2、3、4、5、6、8、9、10ml, 保持溶液总体积为50ml, 其它条件与实验操作同1.4。

1.6 不同温度时VC- $\text{Pb}^{2+}$ 配合稳定常数的测定: 维持MG浓度为 $5.0 \times 10^{-4} \text{ mol/L}$ , 分别测定温度为21、24、26、28、30、32、34、37、 $40^\circ\text{C}$ 时的配合稳定常数, 实验操作同1.4。

## 2 实验结果

2.1 VC加合质子常数: 将方法1.3中消耗的NaOH体积数和pH值变化输入计算机处理, 作生成函数 $h(L) \sim \text{pH}$ 关系曲线, 见图1,  $\bar{n}(L) = (T_H - [\text{H}^+] + [\text{OH}^-]) / T_L$ 。从图1曲线上找出 $\bar{n}(L)$ 为0.5、1.5处的pH值, 即为VC的加合质子常数 $\lg k_1^H = 10.55$ ,  $\lg k_2^H = 4.06$ 。

2.2 VC- $\text{Pb}^{2+}$ 配合稳定常数: 根据Bierrum半整数法 $^{[2]}$ , 生成函数 $\bar{n}$ 与配体浓度 $[L]$ 的关系式为 $\bar{n} = \{ T_L - [L] (1 + \beta_1^H[\text{H}^+] + \beta_2^H[\text{H}^+]^2) \} / T_M$ 。将1.4中消耗NaOH溶液的体积数和pH值变化, 输入计算机处理, 作 $\bar{n} \sim \lg[L]$ 曲线, 见图2。由图2曲线上找出 $\bar{n}$ 为0.5、1.5处的 $\lg(L)$ 值, 即为VC- $\text{Pb}^{2+}$ 配合物的稳定常数 $\lg k_1 = 6.63$ ,  $\lg k_2 = 4.44$ 。

2.3 不同MG浓度时VC- $\text{Pb}^{2+}$ 配合稳定常数: 将1.5中测得的数据输入计算机处理, 得到

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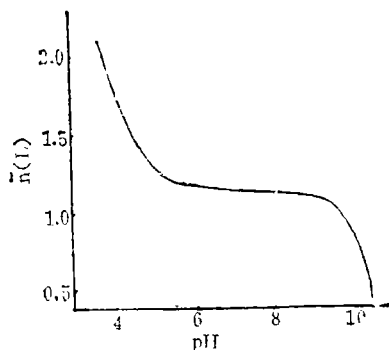


图1 VC-Pb<sup>2+</sup>体系  $\bar{n}$ -pH关系曲线

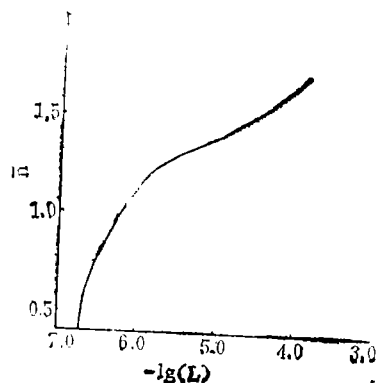


图1 VC-Pb<sup>2+</sup>体系  $\bar{n}$ -lg[L]关系曲线

不同MG浓度时的VC-Pb<sup>2+</sup>配合稳定常数。结果见表1。

2.4 温度对VC-Pb<sup>2+</sup>配合稳定常数的影响:将1.6中测得的实验数据输入计算机处理,得到不同温度时VC-Pb<sup>2+</sup>配合稳定常数,结果见表2。

表1 MG浓度对VC-Pb<sup>2+</sup>配合稳定常数的影响

V <sub>MG</sub> /ml	0	1	2	3	4	5	6	8	9	10
lgk <sub>1</sub>	6.35	6.35	6.40	6.42	6.50	6.57	6.62	6.74	6.85	6.92
lgk <sub>2</sub>	3.32	3.59	3.75	3.90	4.30	4.56	4.56	5.00	5.10	5.15

表2 温度对VC-Pb<sup>2+</sup>配合稳定常数的影响

t/°C	21	24	26	28	30	32	34	37	40
lgk <sub>1</sub>	7.71	7.42	5.08	6.92	6.74	6.77	6.77	6.63	6.48
lgk <sub>2</sub>	5.53	5.05	4.67	4.55	4.45	4.43	4.45	4.44	4.38
lgk <sub>2,1</sub>	9.86	9.57	9.23	9.11	8.98	8.81	8.73	8.72	8.59
lgk <sub>2</sub> *	7.94	7.63	7.27	7.18	7.11	6.97	6.92	6.91	6.76

\*MG的浓度为 $5.0 \times 10^{-4}$  mol/L

### 3 讨论

3.1 为证实本实验方法的可靠性和所用仪器的准确度,我们在25°C条件下测定柠檬酸与铅配合稳定常数lgk = 5.55,实验值与文献基本一致<sup>[3]</sup>。

3.2 实验结果表明,随着MG浓度的增大,VC-Pb<sup>2+</sup>配合稳定常数也增大。为了探论VC-Pb<sup>2+</sup>配位机理,我们对MG-Pb<sup>2+</sup>体系也进行了初步的研究,实验中发现MG与Pb<sup>2+</sup>也发生一定的作用,故所测得的VC-Pb<sup>2+</sup>配合稳定常数为表观配合稳定常数。由此可见,MG的存在能增大VC-Pb<sup>2+</sup>配合稳定常数。

3.3 在MG存在时,VP-Pb<sup>2+</sup>配合稳定常数随温度升高而减小,这和理论上的预测相一致,说明VC-Pb<sup>2+</sup>配合反应为放热反应。以lgk对1/T线性回归,可以看出有MG时的反应热效应明显增大,这也表明,有MG存在的溶液更利于和Pb<sup>2+</sup>发生配合作用。

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# ABSTRACTS OF ORIGINAL ARTICLES

## Studies on the Chemical Constituents of Shellfish *Pricklyash*

(*Zanthoxylum dissitum*)

Tang Jun, Zhu Wei, Tu Zhiben

Eight crystalline compounds were isolated from the stem of *Zanthoxylum dissitum* Hemsl. for the first time. Seven of them were identified as dictamnine (I),  $\gamma$ -fagarine (II), skimmianine (III), 4-methoxy-1-methyl-2-quinolone (IV), haplopine (V),  $\beta$ -sitosterol (VI) and daucosterol (VII) on the basis of spectral data. The eighth was a mixed long-chain fatty (VIII) (mainly  $C_{26}H_{52}O_{22}$ ).

(Original article on page 563)

## Studies on the Chemical Constituents of *Maoruixiang* (*Daphne odora*)

Wang Wei wen, Zhou Bingnan, Wang Chengrui

Four compounds were isolated from the root of *Daphne odora* sp.. Their structures were identified by chemical and spectroscopic methods as daphnoretin, daphneticin, D(-)-lariciresinol and  $\beta$ -sitosterol.

(Original article on page 566)

## Studies on the Chemical Constituents of Japanese Honeysuckle

(*Lonicera japonica*)

Gao Yumin, Mu Huijun, et al

Four flavonoids were isolated for the first time from *Lonicera japonica* Thunb.. Their structures were identified by spectroscopic (IR, UV,  $^1H$ NMR,  $^{13}C$ NMR and MS) and chemical methods as luteolin-7-O- $\alpha$ -D-glucoside (I), luteolin-7-O- $\beta$ -D-galactoside (II), quercetin-3-O- $\beta$ -D-glucoside (III) and hyperoside (IV).

(Original article on page 568)

## On the Quality Standard of Huichunzhibao Oral Liquid (HZOL)

Guo Tao, Jin Baofeng, et al

Huichunzhibao oral liquid (HZOL) is a traditional Chinese herb preparation composed of *Panax ginseng*, Hairy Antler (*Cervus nippon* Temminck) and *Epimedium brevicornum* Maxim.. The active principle of each component was identified by TLC and icariin, the main active principle of *E. brevicornum* was determined quantitatively by HPLC. The method was found to be accurate, sensitive and reproducible with average recovery 98.97% and RSD=1.53 (n=3).

(Original article on page 572)

## Effect of Monoammonium Glycyrrhizinate on

Ascorbic Acid and Lead Complex

Shao Wei, Wang Chunxiang, Mi Guangtai, et al

Stability constant of ascorbic acid and lead complex was measured by pH potentiometry at different temperatures and concentrations of monoammonium glycyrrhizinate (MG). At a concentration of  $5.0 \times 10^{-4}$  mol/L and at biological condition,  $\lg k_1 = 8.72$  and  $\lg k_2 =$

6.91. The result suggested that the stability constant can be improved at decreased temperatures and increased concentrations of MG.

( Original article on page 574 )

## Effects of Six Effective Components of Chinese Herbal Drugs on Calmodulin-Dependent Cyclic Nucleotide phosphodiesterase

Yang Dongli, Gu Xiongfei, et al

Effects of nitidine (Nit), berberine (Ber), sinomenine (Sin), ephedrine (Eph), houttuynin (Hou), quercetin (Que) and trifluoprazine (TFP) on calmodulin-dependent cyclic nucleotide phosphodiesterase (CaM-PDE) were investigated by orthogonal design. Our observation came out that Nit, Que and TFP significantly inhibited the CaM-activated PDE activity ( $P < 0.01$ ) in the order of Que > TFP > Nit. Ber, Eph, and Hou had no effects on the enzyme activity ( $P > 0.05$ ). The effect of Sin on CaM-PDE was uncertain. It was also shown that there were cooperativity between Nit and TFP and synergism between Que and TFP. These results suggested that Nit and Que may act as calmodulin antagonists and might have different sites on calmodulin in comparison with those for TFP.

( Original article on page 582 )

## Inhibition of Respiratory Syncytial Virus by Wuhutang, A Traditional Chinese Prescription Composed of Five Medicinal Herbs

He Shuangteng, Ou Zhengwu, Wu Canrong

Wuhutang, a well known traditional Chinese herbal decoction for the treatment of asthma was found to have an antiviral effect on respiratory syncytial virus (RSV) both in vitro and in vivo. A 50% reduction of plaque formation was observed on Hep-2 cell monolayer at a concentration of 1:80. At such concentration, the value of lg TC ID<sub>50</sub> of viral yield was 2.1, and 55% RNA synthesis of RSV was inhibited. It was found that among the five medicinal herbs in prescription *Ephedra sinica* Stapf is responsible for the antiviral activity on RSV. IC<sub>50</sub> for plaque inhibition was found to be 1.6mg/ml. In animal model, Wuhutang significantly reduced the titre of RSV and accelerated RSV clearance in mice, and alleviated viral pneumonitis by either oral or aerosol route.

( Original article on page 585 )

## Effect of Common Threewingnut (*Tripterygium wilfordii*) on Blood Rheology in Experimental Arthritis Rats

Liang Wenbo, Jin Zhengnan, Piao Huishun, et al

Ethyl acetate extract of *Tripterygium wilfordii* (20mg/kg, 40mg/kg), given to adjuvant arthritis rats (ig) for 7 consecutive days, markedly decreased both high and low shear whole blood viscosity, plasma viscosity, whole blood reduction viscosity, hematocrit and fibrinogen content, but without effect on blood sedimentation and K value in blood sedimentation equation. These results indicated that the decreasing effect of *T. wilfordii* on blood viscosity may be related to its influence on red blood cells and plasma composition.

( Original article on page 589 )