

应用扫描电镜X射线能谱仪定量分析

天然牛黄与牦牛黄和培植牛黄的微量元素

青海省高原医学科学研究所(西宁810012) 叶于聪*

陈钦铭

摘要 应用扫描电镜X射线能谱仪定量分析了9个牛黄样品的微量元素,结果表明天然牛黄含10种微量元素(Na、K、Ca、Mg、Zn、Fe、Cu、P、Cl、S),牦牛黄含8种微量元素(Na、K、Ca、Fe、Cu、Ce、Cl、S),培植牦牛黄含10种微量元素(Na、K、Ca、Mg、Fe、Cu、P、Rb、Cl、S)。这3种牛黄共同含有7种微量元素(Na、K、Ca、Fe、Cu、Cl、S),其间含量差别不大。

关键词 牛黄 牦牛黄 培植牛黄 微量元素 扫描电镜X射线能谱

天然牛黄系名贵而常用的中药。中国药典1977、1985年版一部以及卫生部进口药材部颁标准均将其法定为牛科动物黄牛*Bosttaurus domesticus* Gmelin的干燥胆结石。而来自水牛*Bubalus bubalis* L.的胆囊结石^[1]、牦牛*Bos grunniens* L.的胆囊结石^[2]则分别称之为水牛黄和牦牛黄。牛黄具有清心化痰、利胆、镇惊等功效,其化学组成属于胆红素—胆固醇混合结石类,其中所含的胆酸、胆红素、肽类、微量元素等成分均被认为与其镇静、解痉、退热、解毒、利胆、强心、降压等作用有关的活性成分^[1]。鉴于中药微量元素含量是影响其质量和临床疗效的一个重要因素^[3],而有关天然牛黄的微量元素报道不多,牦牛黄与牦牛培植牛黄的微量元素含量则未见报道,今对青海产天然牛黄、牦牛黄与培植牛黄的微量元素进行对比分析。

1 材料与方法

1.1 天然牛黄:购自青海省医药公司,3个样品的重量分别为15g、21g、24g;测其胆红素含量分别为39.6%、41.4%、45.2%;其总胆酸含量分别为8.45%、9.10%、9.86%。

1.2 牦牛黄:购自青海省同德县医药公司,3个样品的重量分别为13g、19g、25g;测其胆红素含量分别为24.2%、34.1%、36.4%;其总胆酸含量分别为16.57%、9.41%、13.27%。

1.3 牦牛培植牛黄:购自青海省同德县畜牧兽医站,3个样品的重量分别为2.1g、2.7g、4.2g;测其胆红素含量分别为27.2%、28.0%、31.5%,其总胆酸含量分别为19.30%、13.51%和9.36%。

1.4 扫描电镜X射线能谱仪定量分析:将测试样品直接置于挖有直径约2~3mm、深1~2mm的炭棒小洞中,每个炭棒台同时安置3个样品,分别为天然牛黄、牦牛黄与培植牛黄。将样品台送入扫描电镜JEOL-JSM-35CF中,应用EDAX, Serie II, Fracon Northern仪器进行分析,图象及数据由打印机输出。

2 结果

2.1 天然牛黄,牦牛黄与培植牛黄微量元素定量分析:结果见表1。天然牛黄、牦牛黄与培植牛黄的微量元素组成基本相同,且含量差异不超过2倍。它们之间的区别在于:与天然牛黄相比,牦牛黄缺乏镁、锌、磷等微量元素,而培植牛黄仅缺锌元素;另外,牦牛黄中含有

*Address: Ye Yucong, Qinghai Provincial Institute of High Altitude Medical Sciences, Xining

表1 天然牛黄、牦牛黄、培植牛黄中微量元素含量

样 品 号		微 量 元 素 成 分 及 含 量(wt%)											
		Na	K	Ca	Mg	Zn	Fe	Cu	P	Ce	Rb	Cl	S
天然牛黄	1	14.12	1.88	49.11	2.90	2.22	3.66	1.17	3.24			10.32	11.38
	2	18.33	4.21	45.82	3.24	4.11	1.40	2.72	4.28			8.11	7.12
	3	15.94	2.75	47.10	3.08	1.97	1.74	1.21	3.63			11.68	11.10
	$\bar{x}$	16.13	2.95	47.34	3.07	2.77	2.27	1.70	3.92			9.97	9.87
	$\pm SD$	± 2.11	± 1.18	± 1.66	± 0.17	± 1.17	± 1.22	± 0.88	± 0.86			± 1.71	± 2.38
牦 牛 黄	1	18.12	2.03	48.71			1.32	3.92		1.88		12.71	11.39
	2	15.33	1.10	45.11			1.18	2.88		2.68		15.31	16.41
	3	15.71	1.22	45.85			0.94	3.75		2.59		13.45	16.50
	$\bar{x}$	16.38	1.45	46.56			1.15	3.52		2.38		13.82	14.74
	$\pm SD$	± 1.50	± 0.50	± 1.90			± 0.19	± 0.56		± 0.44		± 1.34	± 2.97
培植牛黄	1	18.12	3.12	44.33	3.86		2.24	2.83	3.01		2.02	11.01	9.41
	2	21.91	2.04	40.11	2.96		1.83	2.16	4.41		3.61	16.32	4.65
	3	20.41	2.67	41.46	3.02		1.93	2.35	3.59		2.40	11.19	10.88
	$\bar{x}$	20.15	2.61	42.00	3.28		2.00	2.46	3.67		2.68	12.84	8.31
	$\pm SD$	± 1.91	± 0.54	± 2.14	± 0.50		± 0.21	± 0.37	± 0.70		± 0.83	± 3.02	± 3.26

钨、培植牛黄中含有铷，而天然牛黄中未发现这2种微量元素。

2.2 不同来源天然牛黄微量元素成分的比较：结果见表2。同为天然牛黄，因其来源与黄牛生活地区不同，其微量元素组成虽基本相似，但也有某些差异，主要表现在：北京天然牛黄虽测出18种微量元素，但未测出有钾、镁；福建天然牛黄测出含有9种微量元素，但未测出氯元素；青海天然牛黄测出10种微量元素，但未测出锰元素。由于各作者所采用的测试方法不同，因而无法对每种微量元素的含量进行比较。

表2 不同产地天然牛黄、牦牛黄与培植牛黄微量元素含量比较

作 者	样品	来 源 与 地 产	测 试 方 法	元 素												
				Na	K	Ca	Mg	Zn	Fe	Cu						
王四齐(*) (1985)	天然牛黄	黄牛(北京)	中子活化分析法(ppm)	0.9*		2.4*		524	132	54						
田惠军(*) (1991)	天然牛黄	黄牛(福建)	原子吸收法(μg/g)	4679	2038	11262	183.5	2030	284.4	45.9						
叶于聪(1991)	天然牛黄	黄牛(青海)	EDAS法wt(%)	16.13	2.95	47.34	3.07	2.97	2.27	1.70						
叶于聪(1991)	牦牛黄	牦牛(青海)	同上	16.38	1.45	46.56			1.15	3.52						
叶于聪(1991)	培植牛黄	牦牛(青海)	同上	20.15	2.61	42.00	3.28		2.10	2.46						
元 素																
Mn	Pb	Sb	Cr	Sc	Mo	Sn	Ce	Co	Rb	P	Se	As	S	Hg	Cr	Br
223		0.08	4.0	0.006	0.26	0.02	1.5	0.03			0.09	1.6		0.09	0.5*	4.1*
100.9	91.7									3.92			9.87		9.97	
							2.38						14.84		13.82	
									2.68	3.67			12.84		12.84	

*：为% 非ppm

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通以纯O₂。左心房下端固定于刺激电极上,上端和肌力换能器相连,将心肌收缩信号输至二导仪。左心房由药理,生理多用仪给予3ms,1Hz和1.2倍阈电压方波刺激,以引发收缩,右心房保留窦房结,自发发生收缩,平衡1h后,记录收缩曲线作为对照。然后分次加入天山花楸水煎醇沉液,累积给药,给药间隔3min,每次加药2min后记录收缩曲线。结果,天山花楸水煎醇沉液0.5~31.0mg/L对兔心房呈剂量依赖性负性变力和负性频率作用。

3 讨论

实验结果表明,天山花楸水煎醇沉液具有显著的镇咳、祛痰、平喘作用,这些作用是民间临床治疗咳嗽、痰症、哮喘的药理学基础。此外,发现其乙醇提取液明显抑制离体气管平滑肌收缩并能对抗乙酰胆碱和组织胺引起的支气管平滑肌收缩(待发表)。并且其LD₅₀值较大,可望该药成为一个新的平喘药物。

与一般平喘药不同,天山花楸水煎醇沉液对心脏呈抑制效应。从对心电图的影响看,它使P-P间期延长,P-R间期延长,但QRS综合波变化不大,说明它可能有钙通道阻断作用。

致谢:实习生巴依斯克林,买买提在实验中作了部分工作,在此表示感谢。

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3 讨论

应用扫描电镜X射线能谱仪定量分析微量元素的成分和含量,其原理是样品受到电子束照射时,其中的各元素释放出特有波长的X线,经用探测仪捕获后,转换成相应脉冲,记录后通过换算可以进行定性和定量分析。

应用该法分析牛黄中微量元素的成分和含量,成功的关键在于严格选择样品台,以避免牛黄中可能含有的微量元素与样品台的金属元素成分相混淆,为此,铝合金台(含有铝、镁等元素),铜合金台(含有铜、锌等元素)均不适用,现用特制的炭棒(仅含有碳元素)制成样品台,较为理想。

已有文献报道应用中子活化分析法^[4],原子吸收法^[5]分析牛黄微量元素,上述方法较为复杂,样品用量大。而应用扫描电镜X射线能谱仪进行定量分析,具有方法简便,样品用量少,准确性高,重复性强等优点。近年来对某些微量元素生理活性的研究认为,中药中含锌量高的为寒药,通过进一步研究表明锌元素对生物机体确有清热、凉血、消炎、生肌之功能^[4]。青海产天然牛黄中含锌微量元素,其含量较铜、铁为高,与钾相近似,而牦牛黄与培植牛黄则缺乏锌微量元素,这是否会影响后两者的药理活性有待进一步研究。

通过对不同产地5种天然牛黄微量元素成分的比较分析,发现有5种微量元素是共有的(钠、钙、锌、铁、铜),其中,北京天然牛黄缺乏镁微量元素,而福建与青海天然牛黄则含有镁,已有文献报道认为镁元素与天然牛黄的导滞泻火,清热解毒有关。因此,不同产地天然牛黄因其微量元素成分的不同,是否会影响其药理作用,尚待今后研究。

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(1994-06-27收稿)

ABSTRACTS OF ORIGINAL ARTICLES

Studies on the Antifertility Chemical Constituents of Balsampear (*Momordica charantia*)

Chang Fenggang , Li Jianmei

A protein was isolated by DEAE-cellulose Chromatography and ultracentrifuge from the fruits of *Momordica charantia* L., and identified by chemical and polyacrylamide gel electrophoresis methods. The molecular weight was 34 000; isoelectric point pH 8.4, N-terminal amino acid was leucine. It was composed of 17 kinds of amino acids. The protein has been shown to have antifertility action in male rats.

(Original article on Page 281)

Studies on the Chemical Constituents from the Root of Thistleleaf Adina (*Adina rubella*)

He Zhisheng, Fang Shiyue, Xu Chuanfeng

Eight compounds were isolated from the roots of *Adina rubella* Hance. They were identified as quinovic acid(I), 3-oxo-urs-12-ene-27, 28-dioic acid (II), quinovic acid-3 β -O- β -D-glucopyranoside(III), quinovic acid-3 β -O- α -L-rhamnopyranoside(IV), noreugenin (V), 7-O- β -D-glucosyl-noreugenin(VI), scopolin(VII), daucosterol(VIII), by means of spectral analysis and reactions, II, III and IV are isolated from the genus *adina* for the first time.

(Original article on page 285)

Chemical Constituents of Traditional Chinese Drug Shunk Bugbane (*Cimicifuga foetida*)

Li Congjun, Chen Dihua, Xiao Peigen

Ten constituents have been isolated from the rhizomes of *Cimicifuga foetida* L.. Based on spectral evidence and by direct comparison with authentic samples, they were identified as isoferulic acid(I), 3-acetylcaffeic acid(II), caffeic ester glucoside(III), cimifugin(IV), cimifugin glucoside(V), 6-isoinosine(VI), cimidahurine(VII), cimidahurinine(VIII), D-glucose (IX) and sucrose(X).

(Original article on page 288)

Determination of the Trace Elements Ox-gallstone from Three Sources with EDAX

Ye Yucong, Chen Qinge

Nine samples of OX-gallstone have been studied by scanning electron microscope and energy dispersive X-ray spectrometer. The determinative results indicated that calculus of *Bos taurus domesticus* Gmelin contained ten trace elements (Na, K, Ca, Mg, Zn, Fe, Cu, P, Cl, S), calculus of *B. grunniens* L. contained eight trace elements (Na, K, Ca, Fe, Cu,

Ce, Cl, S), cultivate calculus of *B. grunniens* L. contained ten trace elements (Na, K, Ca, Mg, Fe, Cu, P, Nd, Cl, S). Three species calculus all contained seven trace elements (Na, K, Ca, Fe, Cu, Cl, S), and the differences of their content were no significant.

(Original article on page 293)

The Quantitative Analysis of Trace Germanium in 18 Kinds of Chinese Medicinal Herbs

Liu Yan, Ma Keli, Wang Yin, et al

By digestion with concentration sulfate acid and fuming nitric acid under refluxing coprecipitation with $\text{Fe}(\text{OH})_3$, colorimetry with phenylfluorone-cetyl trimethyl ammonium bromide (CTMAB), germanium (Ge) contents of 18 kinds of Chinese medicinal herbs were determined. The Ge contents in *Ganoderma lucidum* and *oldenlandia diffusa* were higher than those of others (2.46 and 0.35×10^{-8} , respectively). In this method, the recoveries of Ge added to various herbs were in the range of $91\% \sim 93\%$. The detection limit and coefficient variation were 198 ng/g and 0.89% , respectively.

(Original article on page 295)

In Vitro Dissolution Test of Flavonoid Pilulae from Gegen

Guo Jianping, Zhao Tongying, et al

Flavonoid Pilulae from Gegen were prepared by melting method. Using PEG 4000 and PEG 6000 as carrier. Series of studies on the in vitro release kinetics were carried out. PEG 4000 : PEG 6000 ratio had no effect on the release kinetics. PEG 4000 : flavonoids ratio had an evident effect on the release properties of the pilulae, the higher the ratio, the faster the release rate. But when the PEG 4000 : flavonoids ratio exceeded $10:1$, a reverse effect could be seen. Compared with "Gegen flavonoids" tablets, "Yufengxingxin" tablets (release half time, $T_{50} = 94.79 \text{ min}$), the pilulae gave a much fast release characteristic ($T_{50} = 11.56 \text{ min}$).

(Original article on page 298)

Studies on the Pharmacology of Extracts of Tianshan Mountain Mountainash (*Sorbus tianschanica*)

Li Dimin, Chen Jian

It has got good effects that aqueous extracts of *Sorbus tianschanica* Rupr (AQ-ESTR) used for the treatment of chronic bronchitis, Pulmonary tuberculosis and edema etc in folk medicine. The pharmacological experiment showed that AQ-ESTR had antiechoic effect on mice induced by ammonia water, expectorant effect and antiasthmic effect on guinea pig induced by mixture of Ach-histamine. Cardiac Pharmacological experiment also showed AQ-ESTR Produced significant bradycardia in mice. At the dose of 25 mg/kg , AQ-ESTR decreased the heart rate and Prolonged the P-R interval of ECG in vivo, AQ-ESTR decreased the contractive force of isolated atrial muscles rabbits in dose-dependent manner.

(Original article on page 302)