# 1-羟基芘的制备及其质谱光谱解析\*

#### 马 蒋 赵\*\*

(北京市环境保护科学研究所,北京 100037)

**摘要** 报告了由芘制备1-羟基芘的方法,对所得产品进行了元素含量、质谱、核磁共振、紫外光谱、红外光谱和荧光 光谱的分析.确定其组成为 C<sub>16</sub>H<sub>10</sub>O<sub>3</sub>, 羟基在 C<sub>1</sub>位上;解析了质谱图中主要裂解产物的结构;给出特征光谱图,克分 子消光(<sup>1</sup>345nm)为 3822.6.产品为较好的色谱纯品.

关键词 1-羟基芘,芘,质谱,光谱.

1-羟基芘是芘的代谢产物,尿中1-羟基芘 是人体接触多环芳烃的一个灵敏、特异的指 标<sup>(1-3)</sup>,日益引起研究者的关注,但迄今尚无商 品标样,为了满足工作需要,我们由芘合成了 1-羟基芘的化学纯品,本文报告制备方法及产 品的鉴定和结构分析结果.

## 一、1-羟基芘的制备方法

1. 合成路线

由 花起始合成 1-羟基 花, 花为北京化工厂 生产的分析纯试剂, 合成路线如图 1 所示.



2. 芘-1-磺酸钠的制备

将一定量的花溶于6倍重量的四氯乙烷 中,冷至0℃,将计算量的氯磺酸溶在等量的四 氯乙烷中,于 0—5℃ 时滴人花的四氯乙烷溶液 中,并在 10—20℃ 搅拌 15—20h。将生成的灰 绿色糊状物倾入冰水中,减压下蒸去四氯乙烷, 滤去少量未反应的芘。 使在热水溶液中的芘-1-磺酸与计算量的硫酸钠煮沸反应,生成易滤 集的芘-1-磺酸钠盐,产率 90-92%。

元素分析结果表明,碳、氢和硫的含量均符 合要求,结果如表1所示。

表1 花-1-磺酸钠盐的元素分析结果

云表	分析结果(%)			
儿茶	1	2	平均	
с	53.98	54.09	54.03	
н	3.01	3.11	3.06	
s	10.98	11.23	11.10	

注: 理论值 C:63.15% H:2.96% S:10.52%

#### 3.1-羟基芘的合成

在不锈钢筒内加入 20g 氢氧化钠颗粒 和 6 ml 双蒸水,电炉加热至 270℃ 左右使融溶,逐 渐投入研细的花-1-磺酸钠干粉 6g,如温度 合 适搅拌后即冒出烟气;如温度不足则成橙红色 沉淀.完全反应后呈黑色油状物.经搅拌后倾 入水中,得深褐色溶液,呈强碱性,用砂芯漏斗

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\*\* 通信联系人 赵振华

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环

过滤,得胶状灰色沉淀,干燥后用升华法提纯, 产率约为1.6%,若采用真空升华则可将产率 提高至64%,具体条件是1.7g粗制品在260— 300℃下,于1×10<sup>-3</sup>mm汞柱真空中升华,所得 黄色粉末用苯重结晶,即获淡黄色针状结晶,熔

表 2 1-羟基芘的元素分析结果

	分析结果(%)			
JL 53	1	2	平均	
С	87.81	87.97	87.89	
н	4.54	4.55	4.55	

注: 理论值 C: 88.05% H: 4.60%

点为 179℃. 元素分析如表 2 所示, 证明合格。

# 二、结构分析与光学谱图

到目前为止的文献资料中一直未见有1-羟基**芘的结构分析报告,现对**其质谱和核磁共 振波谱进行简要分析,并给出光谱图.

1.1-羟基芘的质谱分析

合成样的质谱图如图 2 所示,表 3 和表 4 分别给出样品分子离子的精细质量数和碳、氢、 氧的组成分析结果. 从上述图、表中可确定 218 为分子离子峰,精细测量的分子量为 218.0766 (表 3)、 C<sub>16</sub>H<sub>10</sub>O 的计算值为

表 3 1-羟基芘的分子离子精细质量数

峰号	氏导数	强度		—————————————————————————————————————	(-D) (-D) (-D) (-D) (-D) (-D) (-D) (-D)
	四重级	测定值	规一化值		线宽度
1	28.7998	15.	0.35	7473.840	5
2	28.8108	730.	17.01	7476.931	14
3	31.8098	22.	0.51	8268.912	5
4	32.7898	81.	1.89	8509.370	9
5	47.3161	26.	0.61	11338.998	6
6	81.5525	58.	1.35	15314.317	7
7	82.0543	12.	0.28	15358.346	4
8	82.9692	256.	5.96	15437.942	11
9	87.0341	13	0.30	15781.824	4
10	93.5262	133.	3.10	16298.576	16
u	94.0305	231.	5.38	16337.107	14
12	94.5357	839.	19.55	16375.501	i <b>6</b>
13	95.0384	336.	7.83	16413.504	15
14	95.5369	15.	0.35	16450.982	6
15	100.0284	16.	0. <b>3</b> 7	16780.096	6
16	109.0351	351.	8.18	17397.523	13
17	109.5306	28.	0.65	17429.990	6
18	161.0405	13.	0.30	20191.286	4
19	162.0449	20.	0.47	20235.904	4
20	163.0546	99.	2.31	20280.490	8
21	164.0617	30.	0.70	20324.685	7
22	186.0432	27.	0.63	21228.314	6
23	187.0519	397.	9.25	21267.213	14
24	188.0579	280.	6.52	21305.805	14
25	189.0668	2287.	53.29	21344.307	22
26	190.0708	565.	13.16	. 21382.416	15
27	217.0675	320.	7.46	22339.990	12
28	218.0766	4292.	100.00	22373.507	18
29	219.0762	669.	15.59	22406.560	13
<b>3</b> G	220.0786	45.	1.05	22439.565	8
<b>3</b> I	224.0289	23.	0.54	22568.227	5

**218.0732,** 偏 差 为 1.56×10<sup>-3</sup>, 相 当 于 15.6 ppm,在允许误差范围内,故可确定其组成为 C<sub>16</sub>H<sub>10</sub>O<sub>•</sub>

滚4 1-羟基芘的分子离子元素组成

质景/由荷	同基准峰 线相比百 分率	直质器	元素			
瓜重/屯何 (m/e)		≌M里 单位差数	C <sub>12</sub> /C <sub>13</sub>	H (1)	0 (16)	
100.0284	0.37	-2.9	8/0	4	0	
161.0405	0.30	1.4	13/0	5	0	
162.0449	0.47	2.4	12/1	5	0	
162.0449	0.47	-2.1	13/0	6	0	
163.0546	2.31	4.3	12/1	6	0	
163.0546	2.31	-0.1	13/0	7	0	
164.0617	0 <b>.70</b>	3.6	12/1	7	0	
164.0617	0.70	-0.9	13/0	8	0	
186.0432	0.63	-3.7	15/0	6	0	
187.0519	9.25	1.6	14/1	6	0	
187.0519	9.25	2.9	15/0	7	0	
188.0579	6.52	-0.3	14/1	7	0	
188.0579				8	0	
189.0668	53.29	0.9	14/1	8	0	
189.0668	53.29	-3.6	15/0	9	0	
190.0708	13.16	-3.0	14/1	9	0	
217.0675	7.46	2 <b>.2</b>	16/0	9	1	
218.0766	100.00	3.5	16/0	10	1	
219.0762	15.59	-0.4	15/1	10	1	
219.0762	15.59	-4.8	16/0	11	1	
224.0289	0.54	2.7	17/0	4	1	

由图 2 和表 4 的资料分析分子离子 为 189 的可能结构 (II) 和分子离子为 163 的 可 能 结



构 (III), 推断 1-羟基**芘 (I)** 的可能裂解过程 是:

2. 核磁共振分析结果

对合成样品用 Bruker AM-500 核磁共振 仪进行了核磁共振谱的分析,分析结果如图 3 所示。

根据图 3 中的 谱图信息确定 羟基取代位置





图 3 1-羟基芘的 'H 核磁共振谱图

在1位.确定依据是: ① 'H 核磁共振谱图的 积分值可见芳环区有 9 个氢,这 9 个氢都有较



好的偶合裂分情况;② 如图示用同核去偶可见 各氢之间的偶合关系,可确定羟基的取代位置 在1位;③如羟基在2位,则应有其邻位的1个 氢的单峰,图中未发现,故排除2位;④如羟基 在5位,则结构有对称中心,9个氢应分为5 组,4组各含2个氢,1组含1个氢,与图中情 况不符;⑤ 图中9个氢分为6组,由低场到高



场各组氢数为: 1,2;2,2;1,1; 且偶合情况好, 內个 AB 系统 2,3 和 9,10, 另 3 个氢相邻的偶 合情况由 4,5,6 氢所致,故确定取代基在1位。

3.1-羟基花的光谱图

文献中除见有1-羟基芘的荧光谱图<sup>[1]</sup>外未 见到其它资料,对本实验合成的样品分别进行

了红外(图 4)、紫外(图 5)和荧光光谱(图 6)的 测定。 红外光谱说明在 3000--3400cm<sup>-1</sup> 有--个强的吸收,显示了羟基的特性.

样品的紫外吸收谱图和样品的荧光激发谱 图基本相同,根据一个物质稀溶液的吸收光谱 和荧光激发光谱的一致,是说明该物质无杂质 (或杂质甚少)、无互变异构作用和无分子缔合 的一个指标<sup>13</sup>,从另一个几面说明所合成标样 的纯度是相当高的。样品吸收光 谱 的 2<sub>max</sub> 为 345nm, 克分子消光( < )为 3822.6.

样品浓度为 0.23 µg/ml, 溶剂为甲醇的 水



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环境科学

名称 土样量-流 速-浓度	<i>k</i> <sub>s</sub> (min <sup>-1</sup> )	<sup>≭</sup> ∞(实测) (mgCu/g土)	<sup>≭</sup> ∞(週论) (mgCu/g土)
0.25-1.5-10	$3.89 \times 10^{-3}$	1.44	1.71
0.25-1.0-10	$2.44 \times 10^{-3}$	1.23	1.71
0.25-0.5-10	1.39×10-3	1.13	1.55
0.25-0.5-15	1.33×10-3	1.59	1.71
0.25-0.5-10	1.39×10-3	1.13	1.55
0.25-0.5-5	1.40×10-3	1.19	1.78

表3 不同条件的 k, x, (共和) 和 x, (理和) 值

随着扩散过程不断深入,扩散速率降低幅度不断增加.流速慢、浓度低,扩散越慢,被利用的内表面就越少<sup>[2]</sup>,实测饱和吸附量就越小;反之,流速大,浓度大,扩散越快,被利用的内表面就越多,实测饱和吸附量就越大.

### 三、 结 语

综上所述, 红壤吸附 Cu 的反应过程始终 受扩散效应的影响,起始为外扩散过程,随后是 内扩散过程.Sapek 在研究土壤吸附 Cu 动力学 时曾指出,整个吸附过程由两部分组成,首先是 Cu<sup>2+</sup> 从溶液向土壤固体外表面的快速扩散,接 着是 Cu<sup>2+</sup> 进入土壤颗粒内细孔的 慢扩 散. Aringhieri<sup>131</sup> 等人在研究土壤吸附 Cu<sup>2+</sup> 和 Cd<sup>2+</sup> 动力学时认为,在连续不断搅拌下,即降 低外扩散的影响下,整个吸附过程由内扩散控 制,而内扩散导致反应速率随吸附量的增加不 断降低. 他们的研究结果与本文的结果十分相 似。

从表3数据还可看出,尽管流速、浓度不等,但其理论饱和吸附量 x<sub>∞</sub>基本相等. x<sub>∞(310</sub>) 小于 x<sub>∞(310</sub>).流速、浓度小,差值就大;反之,流 速、浓度大,差值就小.这一结果是由内扩散效 应所致. 据此也可得出,在某一温度和 pH 条 件下,土壤的真正饱和吸附量为一定值,其几乎 不受流速、浓度因素的影响.本实验方法测得 的饱和吸附量不能视为最大饱和吸附量,只有 排除内扩散效应时的实测饱和吸附量才能认为 是真正的 x<sub>∞</sub>.

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պ<mark>այպետ վարերություն կարերության է հայ հայտարկան անդապետվարկան է</mark>ն էն էն էն էն են են հայտարկան չուններեններ կարերություններ

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射光 谱 时, l<sub>ex</sub> 345nm, 狭 缝 8nm, l<sub>em</sub> 由 350 nm 扫描,狭缝 2nm。

## 三、 结 语

由花起始合成的1-羟基花, 经元素分析、 质谱分析、核磁共振谱图解析证明了确为1-羟 基花;给出了样品的紫外光谱、红外光谱和荧光 激发光谱与发射光谱. 综合这些结果证明合成 物是质量上等的高纯1-羟基花标样. 致谢 马立斌同志对核磁共振谱图、王维 国同志对质谱的裂解过程协助解析,特致谢意.

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well as the operation conditions of the pond.

Abstracts

Key words: waste water, stabilization pond, anaerobic, biodegradation, benthic deposit.

Synthesis of 1-Hydroxypyrene and Its Identific. ation. Ma Jiang zhao (Beijing Municipal Research Institute of Environmental Protection, Beijing 100037): Chin. J. Environ. Sci., 13(4), 1992, pp.27-30

A procedure for the preparation of 1-hydroxypyrene from pyrene was described. Its mass spectrum, nuclear magnetic resonance, infrared, ultraviolet and fluorescence spectra were determined. The results show that the compound thus prepared is a very pure product.

Key words: 1-hydroxypyrene, pyrene.

Research on Leaching Dynamics of Dimethypo in Soils. Li Deping. Jin wei (Institute of Soil Science, Academia Sinica, Nanjing 210008) Chin. J. Environ. Sci., 13(4), 1992, pp.31-34

With reference to OECD-Chemicals Testing Guidelines, laboratory experiments were carried out to examine the leaching dynamics of dimethypo in soils. The results suggest that dimethypo possesses a strong tendency of leaching. Thus, most of the pesticide can leach through the soil columns. With the continuous addition of leaching water, all the pesticide in soil columns can leach out. Soil properties did not show great influence on leaching, while flow rate and temperature exerted remarkable effect on leaching dynamics of dimethypo.

Key words: dimethypo, leaching test, dynamics.

Study on the Degradation of Hydrazine Hydrate in River Water. Sun Hong et al. (Environmental Protection Monitoring Station of Benxi 118000):Chin. J. Environ. Sci., 13(4), 1992, pp. 35-39

Labo ratory studies and monitoring practice in a river demonstrate that the degradation of hydrazine hydrate can be described by the first-order reaction dynamics. Its degradation rate was found to be dependent on water temperature, microorganism, concentration of dissolved oxygen, pH and other conditions. The effect of temperature on the degradation rate could be expressed with the formula:  $K_T = K_{20}$ .  $\theta^{(T-20)}$  Calculation with computer shows that when pH=6, then  $K_{20} = 0.028$  1/h and  $\theta = 1.045$ , when pH=8, then  $K_{20} = 0.021$  1/h,  $\theta = 1.036$ . The degradation coefficient of hydrazine hydrate measured in the experiment carried out in the river was equal to 0.3001/h. **Key words:** hydrazine hydrate, degradation. firstorder reastion dynamies

**Oxidation Dephenolization of Waste Water Catalyzed by Horseradish Peroxidase** Hu Longxing et al. (Shanghai University of Technology 200072): *Chin. J. Environ. Sci.*, 13(4), 1992, pp 40-44

The results of the study on oxidation dephenolization of waste water catalyzed by horseradish peroxidase show that for the treatment of waste waters containing only one of the three phenols (phenol,o-chlorophenol and o-aminophenol), the highest pheanol removal efficiency can be reached at pH values around 7. It was also found that at low (4°C) and high (40°C) temperatures, the removal efficiencies reduced

by about 10%, and in the treatment of waste water containing more than one phenols, there existed synergistic "ffect among various phenols resulting in phenol removal efficiencies as high as 95%.

Key words: phenols, waste water treatment, horseradish peroxidase.

A Study on Modification of the Surface of Coal Ash. Lü Yaojiao, Zhang Jishuang (Hunan University 410082): Chin. J. Environ. Sci., 13(4) 1992, pp.45-47 The modification of the surface of coal ash was achieved by treating the ash with six kinds of surfactants including H-NA, H-R through dry or wet processes of activation. Experiment results indicate that the number of hydroxyl group on the ash surface decreased while corresponding groups of activator increased resulting in the improvement of its property of dispersion in organic medium. The properties of processed PVC and rubber samples with the activated coal ash as filler were greatly improved compared with those products with untreated ash as filler. All the technical targets of the new products, except for the decrease of abrasive wear of rubber, which needs to be further improved, reached or surpass the relevant standards. No doubt, thtis is a new path for making use of the regenerated resource with the advantages of lowering the cost of composite material and protecting the environment.

Key words: coal ash, surface modification, composite material.

Taxonomic System for Environmental Science. Wang Huijun, Chen Jingsheng (Center of Environmental Science, Peking University, Beijing 100871): Chin. J. Environ. Sci., 13(4), 1992, pp. 48-51

A new and more reasonable taxonomic standard for environmental science is introduced based on the systematic anaysis of the synthetic, integrate and inter-disciplinary character of the science and the forms and extent of the synthesis and integration. According to the new standard, environmental science can be regarded as an organic entirety composed of three levels of interrelated discipline groups.

Key words: taxonomic system, environmental science. Application of Enzyme Immunoassay in Pesticide Analysis Li Zhixiang, et al. (Institute of Agro. environmental Protection Tian Jing 300191): Chin. J. Environ. Sci., 13(4), 1992, pp. 51-55

This paper introduces briefly the technique of Enzyme **Im**munoassay and its application in pesticide analysis. The basic types, principles, procedures of development and the prospect of future application and further advancement of Enzyme Immunoassay were discussed.

Key words: pesticides, enzyme immunoassay.

Application of Micronuclues Test in Vicia Faba Root Tips in the Rapid Detection of Mutagenic Environmental Pollutants. Ruan Cuicai, Liang Yu. an, Liu Jinling et al. (Guangxi Cancer Institute, Na. nning 530027): Chin. J. Environ. Sci., 13(4), 1992, pp. 56-59

Micronucleus test in vicia faba root tips was performed for