

## A Note on the Gold-Phosphorus System

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During an investigation of coinage metal phosphides<sup>1</sup> a gold phosphide has been prepared and characterized by X-ray methods.

In earlier investigations of the gold-phosphorus system<sup>2,3</sup> indications have been found for the existence of a phase with the composition  $\text{Au}_2\text{P}_3$ , although conclusive evidence for the exact composition does not seem to have been given as yet. Nevertheless the formula  $\text{Au}_2\text{P}_3$  has been frequently used in the literature. In the present investigation an attempt has been made to prepare this phase by

heating gold strips with red phosphorus in evacuated and sealed silica tubes. Three different samples containing 50, 60, and 67 at. % phosphorus, respectively, have been prepared. The reaction proceeded rapidly and usually resulted in a greyish powder, although, at temperatures around 875°C a product containing well developed crystals about 0.1 mm in size and with a metallic lustre was obtained. Powder diffraction patterns were recorded in Guinier-Hägg type focussing cameras with silicon ( $a=5.43054 \text{ \AA}$ ) as internal calibration standard. The powder photographs consisted of the diffraction pattern of a new phase, together with that of gold in the case of the sample most rich in gold. No variation in line positions with composition could be observed for the new phase, indicating a negligible homogeneity range. Elemental phosphorus is probably the second phase in the two phase equilibrium on the phosphorus rich side. The reason

Table 1. Observed powder diffraction data up to  $\theta=39^\circ$ .  $\text{CuK}\alpha_1$  radiation,  $\lambda=1.54051 \text{ \AA}$ .

$I_o$	$hkl$	$\sin^2\theta_o \times 10^5$	$\sin^2\theta_c \times 10^5$	$I_o$	$hkl$	$\sin^2\theta_o \times 10^5$	$\sin^2\theta_c \times 10^5$
m	020	1137	1139	vw	$35\bar{1}$	22806	22823
m	110	2198	2200	vw	261	23966	23968
w	$11\bar{1}$	3697	3702	vw	152	24169	24150
st-	021	4159	4159	vvw	350	24361	24358
vw	130	4478	4478	vvw	$11\bar{3}$	24829	24825
m	111	6740	6738	vvw	190	24974	24977
vvst	041	7568	7575	m	$20\bar{3}$	25715	25732
st	$20\bar{1}$	7640	7646	m	$28\bar{1}$	25852	25867
m+	220	8796	8801	vvw	191	26488	26479
m	150	9026	9033	vw	222	26934	26954
w+	060	10257	10250	vvw	$35\bar{2}$	27333	27328
vw	$15\bar{1}$	10541	10535	vvw	023	28328	28318
vw	$11\bar{2}$	11247	11243	vw	$42\bar{1}$	28738	28735
m	002	12078	12080	vvw	191	29536	29516
st	240	12216	12218	m	242	30351	30370
vvw	022	13220	13219	w	$40\bar{2}$	30594	30583
m	151	13559	13572	vw	400	30650	30649
m	201	13721	13719	w	0101	31491	31491
m	$22\bar{2}$	14809	14808	m-	$42\bar{2}$	31729	31721
vvw	112	17329	17316		043	31735	31735
w	310	17517	17525	w	281	31960	31940
w	$26\bar{1}$	17888	17895	vw	192	33994	34021
vvw	$15\bar{2}$	18072	18077	w	$26\bar{3}$	35997	35982
st	080	18210	18222	w	$210\bar{1}$	36112	36117
vvw	132	19598	19594	vvw	$35\bar{3}$	37879	37873
vvw	330	19805	19802	vvw	371	38786	38766
vvw	$31\bar{2}$	20479	20495		$39\bar{1}$		38767
w	062	22328	22329				

why phosphorus is not detected in the powder photograph may be the low diffracting power of phosphorus in combination with the small amount present as much of it condenses on cooler parts of the silica tubes.

The symmetry and approximate cell parameters were derived from oscillation and Weissenberg photographs obtained by rotating the crystal around an axis which proved to be the twofold axis of a monoclinic unit cell. The cell dimensions were refined by the method of least squares using a program written by J. Tegenfeldt at this institute. The observed  $\sin^2\theta$  values used in the refinement are given in Table 1. They were obtained from a powder photograph of the sample containing 60 at. % phosphorus. The dimensions of the monoclinic unit cell so obtained are:

$$\begin{aligned} a &= 5.8651 \pm 0.0005 \text{ \AA} \\ b &= 14.435 \pm 0.001 \text{ \AA} \\ c &= 4.6712 \pm 0.0004 \text{ \AA} \\ \beta &= 108.399 \pm 0.007^\circ \\ V &= 375.27 \text{ \AA}^3 \end{aligned}$$

The errors given are standard deviations.

As can be seen in Table 1 the indices for the observed reflexions fulfill the condition  $h+k=2n$  indicating a *C*-centered unit cell. This condition was also verified from Weissenberg photographs of three different layer lines. As no restrictions were found for the occurrence of  $h0l$  reflexions possible space groups are *C2/m*, *Cm*, and *C2*, probably with eight gold atoms in each unit cell. It can also be mentioned that the oscillation photographs showed a tendency for the layer lines with *k* odd to be markedly weaker than the layer lines with *k* even.

The X-ray data given here are probably for the phase previously denoted  $\text{Au}_2\text{P}_3$ , although a correct assignment of the true stoichiometry will have to await a complete structure determination.

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## Flavonoids of *Lotus L.*

### II.\* Synthesis of the Flavonols Corniculatusin and Patuletin

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In a previous paper,<sup>1</sup> the isolation and constitutional elucidation of a new flavonol glycoside, corniculatusin-3-galactoside, from the flowers of *Lotus corniculatus L.* have been described. The constitution 5,7,3',4'-tetrahydroxy-8-methoxy-flavonol-3-*O*- $\beta$ -D-galactoside (Ia) was proposed for the flavonoid, mainly based on spectroscopic evidence. The constitution 5,7,3',4'-tetrahydroxy-6-methoxy-flavonol-3-*O*- $\beta$ -D-galactoside was excluded on the basis of the chemical shift of the A-ring proton in the selectively detrimethylsilylated pertrimethylsilyl ether of the aglycone and the deviation in the melting points of the permethylated derivatives of the aglycone and patuletin.

The synthesis of 5,7,3',4'-tetrahydroxy-8-methoxy-flavonol (Ib) and 5,7,3',4'-tetrahydroxy-6-methoxy-flavonol (Ic), as described in this paper, and comparison of their data with those of the natural aglycone, confirmed the constitution (Ia) of the glycoside.

Many authors have described condensations of unsymmetrically substituted 2,6-dihydroxy- $\omega$ -methoxy-acetophenones with benzoic anhydrides, under Allan-Robinson-Kuhn conditions, leading to isomeric 6- and 8-substituted 3-methoxy-flavones (see, e.g., Ref. 2). Using the same method, but replacing the  $\omega$ -methoxy moiety by a  $\omega$ -benzoyloxy group, the 6- and 8-substituted flavonols were assumed to be attainable. Consequently, 2,4,6-trihydroxy-3-methoxy- $\omega$ -benzoyloxy-acetophenone (II) was prepared from iretol (1-methoxy-2,4,6-trihydroxybenzene) and benzoyloxy-

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