

about 250  $\mu$ . 1-Pentanol-formic acid (98 %)-water (50:50:2.5) and butanol-acetic acid (99 %)-water (60:15:25) were selected as solvents. The pure acids or lactones were dissolved in dry acetone or in water (30 mg/ml), and about 1  $\mu$ l was applied. For detection of the acids the following spray reagents were used:

- 1) For general detection of acids: Bromophenol blue, 0.1 % in methanol. The acids show up as yellow spots on a blue background.
- 2) For detection of phorbic acid lactones: Solution A: A filtered solution of 7.0 g hydroxylamine hydrochloride in 100 ml methanol was mixed with an equal volume of 7.2 % (w/v) potassium hydroxide in methanol, filtered, and then applied. Solution B: 1.0 g of ferric chloride dissolved in 100 ml of an 10 % solution of hydrochloric acid in water.

Before spraying the plates were heated at 100°C for 1/2 hour in order to remove the acids from the developing solvent. Upon cooling the plates were sprayed, first with test solution A, and after drying at room temperature for about 10 min with test solution B. Pink spots revealed the presence of the phorbic acid lactones. 3) For detection of piscidic acid: Solution A: 0.5 g Fast blue salt B dissolved in 100 ml of water, freshly prepared. Solution B: A 0.1 N aqueous solution of NaOH. The chromatograms were sprayed, first with solution A and then with B. Yellow-brown spots revealed the presence of piscidic acid.

*Preparation of acids from plant materials for testing of the method.* 1) *Euphorbia resinifera* Berg. 100 g fresh plant material was homogenized in a Waring blender, mixed with 500 ml of boiling ethanol, and refluxed for half an hour, and filtered. The residue was extracted for one hour with 500 ml of boiling water, pressed, and the extract filtered. The two filtrates were combined, concentrated *in vacuo*, and passed through a column of Amberlite 1 R 45 (OH<sup>-</sup>) for isolation of the anions. After washing with distilled water, the acids were eluted from the column with 0.1 N HCl, whereafter the cations were removed on a column of Amberlite IR 120 (H). The isolated acid mixture was evaporated *in vacuo* to dryness, and the residue dissolved in 5 ml of acetone. This solution was used for the thin-layer chromatography.

2) *Euphorbium*. 10 g of the crude drug *Euphorbium* was extracted with 50 ml of boiling water, filtered and the acid isolated in the same way as above. The residue was dissolved in 2 ml of acetone.

3) *Agave americana* L. 100 g of the fresh plant was worked up in the same way as the corresponding sample of *Euphorbium resinifera*

Berg. The acid mixture was dissolved in 5 ml of acetone.

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## Synthesis of a Pyrite-Type Modification of SiP<sub>2</sub>

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The synthesis of orthorhombic SiP<sub>2</sub> has been reported in a recent note.<sup>1</sup> This material was obtained in a low yield by heating a mixture of the elements, silicon powder and red phosphorus, in a sealed evacuated silica tube in a temperature gradient. The reactant sample was held at about 900°C and the product condensed at about 500°C. The stoichiometry was obtained from a single-crystal X-ray study which showed the phase to be isomorphous with SiAs<sub>2</sub>.

Further studies on the silicon-phosphorus system have revealed the existence of one more intermediate phase. This was collected in low yield from a somewhat higher

Table 1. Guinier powder pattern of cubic  $\text{SiP}_2$ ,  $\text{CuK}\alpha_1$  radiation. Internally calibrated with Si ( $a = 5.4310 \text{ \AA}$ ).

$d(\text{obs}) \text{ \AA}$	intensity	$\sin^2\theta(\text{obs})$	$hkl$	$\sin^2\theta(\text{calc})$
		$\times 10^3$		$\times 10^6$
2.851	st	7297	2 0 0	7291
2.551	v st	9116	2 1 0	9114
2.328	st	10945	2 1 1	10936
2.017	m	14584	2 2 0	14582
1.902	v w	16399	3 0 0	16404
1.720	v st	20054	3 1 1	20050
1.648	w	21847	2 2 2	21872
1.582	st	23705	3 2 0	23695
1.525	v st	25511	3 2 1	25518
1.427	v w	29147	4 0 0	29163
1.384	v w	30972	4 1 0	30986
1.345	v v w	32792	4 1 1	32809
1.309	v w	34620	3 3 1	34631
1.276	v w	36436	4 2 0	36454
1.216	w	40116	3 3 2	40099
1.164	w	43779	4 2 2	43745
1.141	v w	45558	5 0 0	45568

region of temperature (approximately  $600^\circ\text{C}$ ), after prolonged heating of the reaction tube described above. The material consisted of tiny crystal cubes (up to  $0.2 \text{ mm}$  on an edge) with a lustre similar to that of silicon. The X-ray Guinier powder pattern listed in Table 1 could be indexed by assuming a cubic unit cell with  $a = 5.705 \text{ \AA}$ .

The symmetry was confirmed by single-crystal Weissenberg photographs taken with  $\text{CuK}$  radiation. A crystal-structure analysis showed the atomic arrangement to be of the pyrite type, suggesting the composition of the phase to be either  $\text{SiP}_2$  or  $\text{Si}_2\text{P}$ . The very short distance within the atom doublet and also other structural considerations were thought to favour the former stoichiometry. It was felt desirable, however, to confirm the composition also by chemical analysis.

The very small amount of the material obtained in the synthesis made it impossible to perform an analysis by conventional methods. An analysis of individual crystals by means of the X-ray microprobe technique was, however, found to be very well suited to the present problem. This analysis was performed in cooperation with Dr. J. Malmqvist using the ARL-AMX instrument of the *Geological Survey of Sweden*. The results obtained for five different crystals, including the one used for the crystal-structure determination, were

Table 2.

Space group:  $Pa\bar{3}$  (No. 205)

$$D_x = 3.23 \quad D_m = 3.15 \quad Z = 4$$

Reliability index (after five cycles of least squares refinement): 0.06

$$4 \text{ Si in } (4b) \quad B = 0.93 \pm 4 \text{ \AA}^2$$

$$8 \text{ P in } (8c) \quad x = 0.3906 \pm 4$$

$$B = 1.03 \pm 5 \text{ \AA}^2$$

Interatomic distances:

P—P:  $2.16 \text{ \AA}$ , Si—6P:  $2.36 \text{ \AA}$ , Si—12Si:  $4.03 \text{ \AA}$

in good concordance and gave an average composition of the substance of 32.5 weight % of silicon and 65.5 % of phosphorus. The values required by the formula  $\text{SiP}_2$  are 31.9 and 68.1, respectively.

The results thus obtained by the crystal structure study and the chemical analysis give the structural data listed in Table 2.

The pyrite structure of  $\text{SiP}_2$  may be visualized as a three-dimensional network of silicon octahedra, each of which with a pair of phosphorus atoms inside. The Si atoms have an extraordinary type of coordination with six P atoms arranged as a regular octahedron. The environment of the P atoms is a tetrahedron consisting of one P and three Si atoms. This structure type is entirely different from that of the orthorhombic modification of  $\text{SiP}_2$ , which contains four-coordinated Si and three-coordinated P atoms. The interatomic distances within the two modifications differ in a way consistent with the structural divergence.

Very recently, Osugi *et al.*<sup>2</sup> reported on the reaction of silicon and phosphorus at high temperatures and high pressures. At  $1100\text{--}1500^\circ\text{C}$  and  $20\text{--}40 \text{ kbar}$  a phase was prepared described as pyrite-type  $\text{SiP}_2$  with a lattice constant  $a = 5.682 \text{ \AA}$ . No analytical data were given and the assignment of the structural type was from X-ray powder patterns only. The material should, however, obviously be the same as that found in the present study. Osugi *et al.* described their product as a high-pressure phase and gave a minimum pressure of formation of about  $20 \text{ kbar}$ . This is not in agreement with the present findings, which have demonstrated the possibility of preparing pyrite-type  $\text{SiP}_2$  at rather low pressures, probably about  $10 \text{ bars}$ . It is interesting to note that the rather dense and high-coordinated pyrite-type phase of  $\text{SiP}_2$  can form at such low pressures.

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## Chemical Studies on Lichens

### 5.\* Separation and Identification of the Antipodes of Usnic Acid by Thin Layer Chromatography

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A thin layer chromatographic method to investigate different lichens as to their content of (+) or (-) usnic acid has been worked out. It was not possible to resolve the acid chromatographically by using methanol containing brucine, the base earlier used for the resolution of the racemic acid.<sup>1</sup> The same negative result was also obtained when two solutions, each containing brucine and (+) or (-) usnic acid, were used. Each solution yielded one spot and the two spots had identical  $R_F$ -values. It was then found that a chromatographically resolvable brucine ( $\pm$ )-usnate was not formed just by mixing the two compounds. For the formation of such a salt or complex heating was necessary, a fact indicating that some kind of reaction must first take place between brucine and usnic acid. When the heat-treated solution was applied on the chromatographic plate and developed with methanol, two spots were

obtained. One spot travelled with the methanol front and was identified as brucine (-)-usnate. The other one had a lower  $R_F$ -value and was a mixture of brucine and brucine (+)-usnate. If the solvent front was allowed to travel more than 4 cm, the brucine (+)-usnate was slowly eluted from the brucine spot and the difference in the  $R_F$ -values of the usnates became too small for their identification. Evidently their chromatographical resolution is due to the fact that only brucine (+)-usnate is forming some kind of complex with brucine resulting in a decrease in its  $R_F$ -value. The nature of this complex is still obscure.

A useful reagent for usnic acid as well as for brucine-usnate is an aqueous solution of titanium trichloride. It forms a gray-green complex with usnic acid and develops a yellow-green colour on chromatographic plates. This reagent was also used to detect usnic acid in lichens with the "filter paper" method.<sup>2</sup>

*Experimental.* The thin layer chromatography was carried out on Eastman "Chromagram sheets" type K 301 R 2, cut down to a height of 6.7 cm. The plates were activated at 100° for 30 min and stored over silica gel. The spots were applied 1.0 cm above the lower edge and the solvent was allowed to travel to a height of 4 cm. (-)-Usnic acid was isolated from *Cladonia alpestris* and (+)-usnic acid from *Cladonia silvatica*.

The following solutions were used:

- (-)-Usnic acid in acetone (saturated) (A)
- (+)-Usnic acid in acetone (saturated) (B)
- Brucine in methanol (0.1 g/ml) (C)

Spots of brucine-usnate were detected either by their dark colour in UV-light (365 nm) or by the yellow-green colour produced by spraying the plates with an aqueous solution of titanium trichloride (10 %).

No resolution was obtained when A or B were chromatographed with C as solvent. Each solution yielded one spot and the two spots had identical  $R_F$ -values. The same result was obtained with either a mixture of A (0.1 ml) and C (0.2 ml) or of B (0.1 ml) and C (0.2 ml), using C or methanol as solvents. Simultaneously, the two mixtures (A + C and B + C) were warmed on the steam-bath until half of the solvent had evaporated. On cooling some of the brucine (+)-usnate was precipitated (from B + C) and the solution was filtered. No precipitate of brucine (-)-usnate was formed. When the solutions were chroma-

\* Part 4. *Acta Chem. Scand.* **21** (1967) 1162.