about 250 μ 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 μl 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 hydroxyamine 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 ferrie 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−) for isolation of the anions. After washing with distilled water, the acics 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.

Acknowledgement. The author is indebted to Professor Dr. Egon Stahl, Institute for Pharmacognosy and Analytical Phytochemistry, University of the Saar, in whose laboratory the present investigation was carried out, and to Professor Dr. Arnold Nordal, Institute of Pharmacy, University of Oslo, who supplied the samples of phorpic and piscidic acid used for the investigation.


Received March 29, 1967.

Synthesis of a Pyrite-Type Modification of SiP₂

TOMMY WADSTEN

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The synthesis of orthorhombic SiP₂ has been reported in a recent note.¹ 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 SiAs₂.

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

Acta Chem. Scand. 21 (1967) No. 5
Table 1. Guinier powder pattern of cubic SiP₄, CuKα₁ radiation. Internally calibrated with Si (a = 5.4310 Å).

Table 2.

Space group: Pn3 (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

<table>
<thead>
<tr>
<th>4 Si in (4b)</th>
<th>8 P in (8c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B = 0.93 \pm 4 ) Å²</td>
<td>( z = 0.3906 \pm 4 )</td>
</tr>
<tr>
<td>( B = 1.03 \pm 5 ) Å²</td>
<td></td>
</tr>
</tbody>
</table>

Interatomic distances:

P–P: 2.16 Å, Si–6P: 2.36 Å, Si–12Si: 4.03 Å

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 SiP₄ 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 SiP₄ 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 SiP₄ 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. reported on the reaction of silicon and phosphorus at high temperatures and high pressures. At 1100–1500°C and 20–40 kbar a phase was prepared described as pyrite-type SiP₄ with a lattice constant \( a = 5.682 \) Å. 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 kbar. This is not in agreement with the present findings, which have demonstrated the possibility of preparing pyrite-type SiP₄ at rather low pressures, probably about 10 bars. It is interesting to note that the rather dense and high-coordinated pyrite-type phase of SiP₄ can form at such low pressures.

Acta Chem. Scand. 21 (1967) No. 5
This investigation was carried out within a research program financially supported by the Swedish Natural Science Research Council. Thanks are due to Dr. A. Danielsson of the Geological Survey of Sweden for the use of the microprobe instrument and also to Professor A. Magnéli for valuable discussions.


Received April 20, 1967.

Chemical Studies on Lichens

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

GERD BENDZ, GERALD BOHMAN and JOHAN SANTESSON

The Institute of Chemistry, University of Uppsala, Uppsala, Sweden

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.1 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 RF-values. It was then found that a chromatographically resolvable brucine (±)-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 RF-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 RF-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 RF-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.2

Experimental. The thin layer chromatography was carried out on Eastman “Chromagram sheets” type K 301 B 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 stellaris.

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 RF-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-