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Crystallographic data of carboxylic acids and carboxyamides of picoline and pyrazine derivatives. By CHIHIRO TAMURA and HARUMITSU KUWANO, *Takaminé Laboratory, Sankyo Co. Ltd., Shinagawa, Tokyo, Japan*, and YOSHIO SASADA, *Institute for Protein Research, Osaka University, Kita-ku, Osaka, Japan*

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Crystal structures of mono-acids and amides of planar six-membered ring compounds have been reported; for example, benzoic acid (Sim, Robertson & Goodwin, 1955), benzamide (Penfold & White, 1959), nicotic acid (Wright & King, 1953), nicotinamide (Wright & King, 1954) and α -pyrazinamide (Takaki, Sasada & Watanabé, 1960). Systematic X-ray examinations on related compounds have been attempted to see relationship among these crystals in molecular arrangement and in hydrogen bond system.

Crystallographic data has been found for picolinic acid,

granule, obtained by pouring hot nitrobenzene solution of this material at 80–140 °C. into tetrachloromethane at room temperature and confirmed by using Debye method. Physicochemical research on these modifications is in progress.

The existence of several modifications of carboxyamides found in the above-mentioned experiments will probably be due to the difference of the possible linking configurations of hydrogen bond systems.

We wish to express our thanks to Mr M. Matsui, Mr

Table 1. *Crystallographic data of carboxylic acids and carboxyamides of picoline derivatives*

	Picolinic acid C ₆ H ₅ O ₂ N	Pyrazinic acid C ₅ H ₄ O ₂ N ₂	Picolinamide C ₆ H ₆ ON ₂	β -Pyrazinamide C ₅ H ₅ ON ₂	γ -Pyrazinamide* C ₅ H ₅ ON ₂
M.p. (°C.)	135–137 sub.	213 decomp.	107–108	187–189	185–189
<i>a</i>	13·97 Å	11·37 Å	16·29 Å	10·70 Å	10·84 Å
<i>b</i>	3·84 Å	6·46 Å	7·15 Å	3·73 Å	3·75 Å
<i>c</i>	10·62 Å	7·38 Å	5·22 Å	14·38 Å	7·20 Å
β	107·9°	—	99·8°	101·7°	106·9°
<i>V</i>	542·5 Å ³	541·7 Å ³	599·7 Å ³	561·9 Å ³	280·1 Å ³
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>Pnma</i> or <i>Pna</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>Pa</i>
<i>Z</i>	4	4	4	4	2
<i>D</i> _c (g.cm. ⁻³)	1·51	1·52	1·35	1·45	1·46
<i>D</i> _o (g.cm. ⁻³)	1·48	1·53	1·4	1·45	1·46

* Takaki *et al.* (1960) named this modification β .

picolinamide, pyrazinic acid and other modifications of pyrazinamide. The lattice constants and the space groups were obtained from oscillation and Weissenberg photographs (Table 1):

(I) *Picolinic acid*, crystallized in rectangular form by sublimation, showing frequently twinning.

(II) *Picolinamide*, recrystallized from ethanol solution at 0 °C.

(III) *Pyrazinic acid*, crystallized from aqueous solution at room temperature. The crystal turned slightly red by oxidation.

(IV) *Pyrazinamide*, at least four forms. α -form, obtained from alcoholic solution at room temperature (Takaki, Sasada & Watanabé, 1960). β -form, obtained in needle from alcoholic solution at about 0 °C. γ -form, obtained from melt in rectangular shape. δ -form, silvery

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Kristallstruktur von β' Cu–12% Al. Von G. THOMAS, *Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley 4, California, U.S.A.* und M. C. HUFFSTUTLER, JR., *Materials Science Laboratory, University of California, Berkeley 4, California, U.S.A.*

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Die Frage der Kristallstruktur der martensitischen β' Phase der eutektoiden Legierung in dem System Cu–Al bedarf immer noch einer genaueren Klärung (Hunger & Dienst, 1960; Tarora, 1949). Martensitische Phasen entstehen im allgemeinen durch kleine Schubverzerrungen

des ursprünglichen Gitters. Aus diesem Grunde sind die Ergebnisse von Hunger & Dienst (1960) zweifelhaft, da die von ihnen gefundenen Gitterkonstanten eine beträchtliche Umordnung erfordern würden. Aus den bekannten Gitterkonstanten der β_1 Phase (Tarora, 1949) und den

Orientierungsbeziehungen der β' Phase (Wassermann, 1934) würde man ein hexagonales Gitter der martensitischen Phase mit $a=2,6$ und $c=4,2$ Å erwarten.

Mittels eines GE XRD-3 Goniometers und Cu $K\alpha$ Strahlung wurden an einem vielkristallinen dünnen Blech die Gitterkonstanten des martensitischen Gefüges (vgl. Ergebnisse in Tabelle 1) zu $a=2,57$ und $c=4,21$ Å be-

Tabelle 1. Vergleich der Gitterkonstanten von β'

	Elektronen- beugung	Röntgen- beugung
Hunger-Dienst	$a=5,16$ Å —	$a=5,16$ Å $c=6,35$
Diese Arbeit	$a=2,57$ $c=4,21$	$a=2,57$ $c=4,21$

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Crystallographic data for gelsemicine hydrobromide hemihydrate and N-methyl-gelsemicine hydrobromide tetrahydrate. By MARIA PRZYBYLSKA, *Division of Pure Chemistry, National Research Council, Ottawa, Canada*

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Gelsemicine was isolated from the root of *Gelsemium sempervirens* Ait. by Chou (1931) and by Forsyth, Marrian & Stevens (1945). Schwartz & Marion (1953) isolated it again and assigned the empirical formula $C_{20}H_{26}O_4N_2$. With a view to carrying out the structural determination, the crystals of gelsemicine hydrobromide hemihydrate and of N-methyl-gelsemicine hydrobromide tetrahydrate were examined.

The hydrobromide hemihydrate, m.p. 146–148 °C. was prepared by Dr S. McLean, who also carried out the determination of the optical rotation and found it to be

$$[\alpha]_D^{25} = -99^\circ \text{ (c, 1.56 in methanol) .}$$

The results of the chemical analysis carried out by Mr R. H. Séguin were: C, 53.76; H, 6.28%. The calculated values for $C_{20}H_{26}O_4N_2 \cdot HBr \cdot \frac{1}{2}H_2O$ are: C, 53.57; H, 6.30%.

The crystals were crystallized from a mixture of methanol and ethyl acetate. They were colourless, but became yellowish on standing. They were found to belong to the monoclinic system and the unit-cell dimensions measured from X-ray precession films taken with Cu $K\alpha$ radiation are:

$$a = 9.18 \pm 0.02, \quad b = 27.60 \pm 0.03, \quad c = 8.98 \pm 0.02 \text{ Å ,}$$

$$\beta = 115^\circ 35' \pm 20'.$$

The crystals were elongated along the a axis, with (010) and (001) faces prominently developed. The linear absorption coefficient for Cu $K\alpha$ radiation is $\mu = 31.9 \text{ cm.}^{-1}$. The density measured by flotation using a mixture of toluene and carbon tetrachloride was found to be 1.43 g.cm.^{-3} , the calculated value for the hemihydrate being 1.45 g.cm.^{-3} .

Since the only systematically absent reflexions were $0k0$ when k is odd, it could be concluded that the space group is $P2_1$ or $P2_1/m$. Since the compound is optically active, the space group must be $P2_1$. There are four molecules per unit cell; hence two molecules constitute the asymmetric unit of this structure.

N-methyl-gelsemicine hydrobromide tetrahydrate,

stimmt. Die Zusammensetzung der Probe (25,1 at.% Al) zeigt dass die β' und nicht die γ' Phase bei Abschreckung formen sollte.

Transmissions-elektronenmikroskopische Untersuchungen (einschliesslich Beugung) zeigen das Vorhandensein von feinen Zwillingen im Martensit, die zusätzliche Beugungspunkte geben. Dies könnte eine mögliche Erklärung der Ergebnisse von Hunger & Dienst (1960) sein. Unsere Resultate bezüglich der elektronenmikroskopischen Untersuchungen werden an anderer Stelle veröffentlicht werden.

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$C_{21}H_{29}O_4N_2Br \cdot 4H_2O$, was prepared by heating gelsemicine in a sealed tube at 60–70 °C. for six hours with an excess of methyl bromide dissolved in methanol. The reaction mixture was then filtered, evaporated to small volume, and diluted with acetone. The crystals which separated were colourless, orthorhombic prisms elongated along the c axis, with easy cleavage on (001). The unit-cell constants are:

$$a = 18.25 \pm 0.03, \quad b = 28.46 \pm 0.05, \quad c = 9.60 \pm 0.02 .$$

The systematic absences are $h00$ and $0k0$ for odd values of h and k respectively and the space group is uniquely determined as $P2_12_12$. Since there are eight molecules per unit cell, there are two molecules of this compound in the asymmetric unit. The density calculated for the tetrahydrate is 1.40 g.cm.^{-3} , compared with the value 1.41 g.cm.^{-3} measured by flotation using toluene and carbon tetrachloride mixture at 25 °C. The absorption coefficient for Cu $K\alpha$ radiation is $\mu = 28.6 \text{ cm.}^{-1}$.

The chemical analysis confirmed that the compound is a tetrahydrate. (Found: C, 48.14; H, 6.65%; Calc.: C, 48.00; H, 7.10%.)

Since the asymmetric units of both these compounds consist of two molecules, no further work on either is contemplated. The crystals of N-methyl-gelsemicine hydriodide which were subsequently prepared did not present this difficulty and were chosen for a detailed X-ray analysis.

I am very grateful to Dr Léo Marion for the sample of gelsemicine and to Dr S. McLean for the preparation of both derivatives. I also wish to thank Mrs C. Mackey for her assistance.

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