

Orientierungsbeziehungen der  $\beta'$  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  $\beta'$

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

*Acta Cryst.* (1961). **14**, 694

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

(Received 24 January 1961)

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  $1.43 \text{ g.cm.}^{-3}$ , the calculated value for the hemihydrate being  $1.45 \text{ g.cm.}^{-3}$ .

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  $\beta'$  und nicht die  $\gamma'$  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.

#### Literatur

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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  $1.40 \text{ g.cm.}^{-3}$ , compared with the value  $1.41 \text{ g.cm.}^{-3}$  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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