ART. X. — *β -Bromvalerianic Acid*, $\text{CH}_3\text{-CH}_2\text{-CHBr-CH}_2\text{-COOH}$; by JOHN G. SPENZER, Cleveland, O.

THE first step in the preparation of β -bromvalerianic acid was the preparation of propylideneacetic acids by the action of hot, caustic soda solution on ethylidene propionic acid.

To one volume of pure propylideneacetic acid contained in a small cylinder having a well ground stopper, $1\frac{1}{2}$ volumes of hydrobromic acid saturated at 0° C. were added, on shaking a clear solution resulted, it was allowed to remain quietly for 24 hours at the ordinary temperature; the monobromide had now risen to the surface of the hydrobromic acid as a light brown colored layer. The cylinder was now vigorously shaken from time to time, to bring any unaltered propylideneacetic acid, which might be dissolved in the monobromide into intimate contact with the hydrobromic acid. After this occasional shaking had been continued for four or five days, the contents of the cylinder formed two distinct layers, the reaction was ended and all the propylideneacetic acid had been quantitatively changed into β -bromvalerianic acid. The cylinder still stoppered was now placed in ice water, to cause the new acid to solidify, this, however, did not occur; it was then placed in a freezing mixture of ice and salt, and on agitating slightly the monobromide at once congealed to a solid mass of fine needles lying on the surface of the hydrobromic acid. The cylinder stood for 15 hours at a temperature of 15° C.; then the crystalline cake was broken through with a glass rod, distributed through the hydrobromic acid and brought into a platinum cone, where it was allowed to dry, being washed with small successive portions of ice water, in order to remove the greater part of the mineral acid.

The contents of the cone were now brought on to a watch glass and placed in a vacuum over sulphuric acid and caustic potassa; a dry sandy, white substance resulted, which was powdered and recrystallized out of petroleum ether. So produced, the β -bromvalerianic acid is, after drying, perfectly pure, as the analysis proves:

0.233 g. of the substance dried in a vacuum gave 0.2410 Ag Br.

Calculated for $C_5H_9BrO_2$.

44.20% Br.

Found.

44.20% Br.

β -bromvalerianic acid melts at 59° to 60° C., the melting point not altering in the least by repeated determinations on the same sample. It dissolves readily in ether, chloroform, carbon disulphide, less easily in benzene and petroleum ether, and is almost insoluble in water of 0° C. If the cold, saturated solution of the monobromide in petroleum ether be allowed to evaporate spontaneously it crystallizes out in beautiful, colorless, 8-sided prisms.

The crystals set up after Naumann's System give the following crystallographic measurements:

β -Bromvalerianic acid.

Crystal system : Monosymmetric.

$\bar{a} : \bar{b} : \bar{c} = 1.4688 : 1 : 0.4900$

$\beta = 79^\circ 58' 45''$

Observed forms: $m = \{110\} \infty P$, $a = \{100\} \infty P \infty$, $b = \{010\} \infty P \infty$, $r = \{011\} P \infty$, $\bar{d} = \{\bar{1}01\} + P \infty$, $e = \{101\} - P \infty$

The crystals are mostly 2 to 5^{mm} long by 1 to 2^{mm} wide and possess a valerianic acid like odor.

Some crystals are without $\{\bar{1}01\} + P \infty$, as also $\{100\} \infty P \infty$, while $\{101\} - P \infty$ was only observed once.

The faces were almost always smooth and polished giving excellent reflections.

The following angles were measured and calculated:

		Measured.	Calculated.
$r : r = (011) : (011)$		$*51^\circ 31'$	-----
$a : m$	$(100) : (110)$	$*55 \quad 21 \quad 30''$	-----
$r : m$	$(011) : (\bar{1}00)$	$*99 \quad 1$	-----
$m : m$	$(110) : (1\bar{1}0)$	110 43	$110^\circ 41'$
$m : b$	$(110) : (010)$	34 47	34 39 30''
$r : b$	$(011) : (010)$	64 6	64 14 30
$a : b$	$(100) : (010)$	89 58	90
$a : \bar{d}$	$(100) : (\bar{1}01)$	99 2	99 12
$r : m$	$(011) : (1\bar{1}0)$	74 2	74 26
$a : e$	$(100) : (101)$	61 59	62 44
$r : \bar{d}$	$(011) : (\bar{1}01)$	36 33	36 29
$r : m$	$(011) : (110)$	63 33	63 28
$r : \bar{d}$	$(011) : (\bar{1}01)$	31 8	31 45
$\bar{d} : m$	$(\bar{1}01) : (\bar{1}00)$	80 11	80 48

The plane of the optical axes stands at right angles to the clinopinacoid and is only slightly inclined towards the orthopinacoid.

A cleavage could not be found. Obtuse bisectrix = $\bar{b}$ axis.