RHAMNONIC LACTONE 1,4 AND 1,5. CRYSTALLOGRAPHICAL AND OPTICAL PROPERTIES

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The crystals of the two rhamnonic lactones, whose crystallographic and optical properties are described in this paper, were prepared by Drs. Ernest L. Jackson and C. S. Hudson[1] from a solution in acetone. The 1,5-crystals are smaller than the 1,4-crystals and are more perfectly developed. The 1,5-crystals proved to be the crystals described by Will and Peters[2] in their work on rhamnonic lactone.

Rhamnonic Lactone 1,5.—Crystallized from solution in acetone. Crystal system, orthorhombic, class bisphenoidal; axial ratio, $a:b:c$ = 0.6874:1:1.2592. Two different lots of crystals were available for measurement.

Crystals of the first lot are in the form of short, stocky prisms 1 to 3 mm. long and 0.5 to 1 mm. thick. They are bounded by the forms (110), (010) and (101) chiefly; the forms (100), (012), (001), (111) occur as smaller facets; form (021) is rare and was observed only on a single crystal; the basal pinacoid is never well developed. The crystals are commonly grouped together in clusters and radiate from a common center; six or eight crystals may be so arranged. Some of the crystals are doubly terminated; but most of the crystals are attached at one end to a cluster and exhibit crystal faces only at the free end. On some of the crystals the end faces are symmetrically developed; but a number show a tendency toward unequal growth of the dome faces 101 and $\bar{1}01$, also 011 and $0\bar{1}1$. The forms (110) and (101) on many crystals exhibit small, beautiful etch figures that emphasize the sphenoidal hemihedrism of the crystals. The etch figures on 101 are three-sided with curved boundaries (Fig. 1) and with one of the sides parallel with the edge between 101 and $1\bar{1}0$; similarly the etch figures on 110 are three-sided with curved boundaries and with one side parallel with the edge between 110 and 101. Etch figures were not observed on the prism face $1\bar{1}0$.

In the second lot of crystals the form is more nearly equant, and the tendency to form clusters is less pronounced. The crystals are doubly terminated and range from 1 to 2 mm. in length and somewhat less in thickness. They are bounded by the forms (110), (010), (101), (011) and (012) chiefly; the pyramid (111) appears as small triangular facets; the forms (010) and (001) are less prominent with (001) poorly developed or failing altogether. No face is etched. The shape of the crystals is shown in Fig. 2.

[1] Their article immediately precedes the present paper.

[2] Will and Peters, *Ber.*, **22**, 1704 (1889).

The fracture is conchoidal; no cleavage was observed.

Six carefully selected 1,5-crystals were measured on a Goldschmidt two-circle goniometer with reducing attachment. Many of the observed reflection signals were single and excellent; many were multiple and poor. The average of 8 best unit prism angles thus obtained is 69°00′ with departures of ±1′ from the mean. The average polar distance ρ for the form (101) is 61°22′, the values measured on 10 faces ranging from 61°13′ to 61°31′. For (011) the mean polar distance is 51°33′ for 7 faces, the observed angles ranging from 51°22′ to 51°40′. The axial ratios were

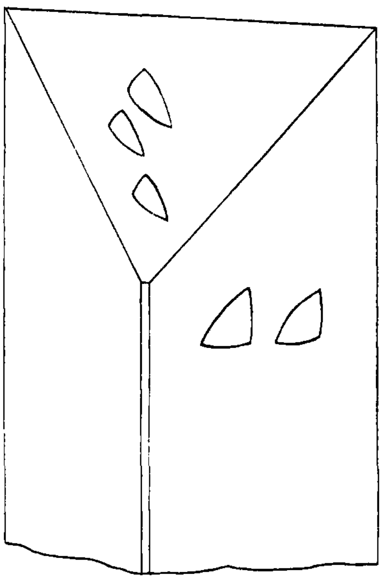

Fig. 1.—Etch figures observed on the forms (110) and (101) of rhamnonic lactone-1,5.

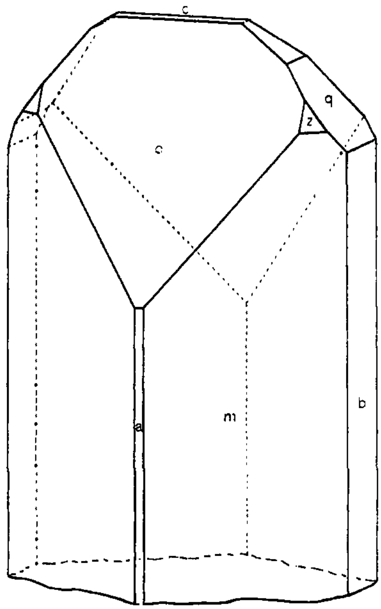

Fig. 2.—Crystal of rhamnonic lactone-1,5.

computed by the systematic two-circle method for all satisfactory faces. On the basis of the values thus obtained the table of angles for this form is as follows.

Crystals of the 1,5-substances were also obtained from a solution in alcohol. These crystals are in the form of needles and clusters of needles of subparallel arrangement. The prism faces on some of the crystals are sufficiently developed to permit measurement on the goniometer; their interfacial angle is 69°00′, characteristic of the form (110). The terminal facets are invariably rounded and yield no reflection signals. Many of the needles taper at the end and show no terminal faces.

Under the microscope and between crossed nicols all 1,5-crystals extinguish parallel with the elongation. Birefringence is strong. Sections

TABLE I

RHAMNONIC LACTONE 1,5

$a = 0.6874$ $a_0 = 0.5459$ $p_0 = 1.8319$
$c = 1.2592$ $b_0 = 0.7942$ $q_0 = 1.2592$

No.	Letter	Symb. Crdt.	Miller	φ	ρ	ξ_0	η_0	ξ	η	x Prisms x:y	y	d tanρ
1	c	0	001	....	0°00′	0°00′	0°00′	0°00′	0°00′	0	0	0
2	b	0 ∞	010	0°00′	90 00	0 00	90 00	0 00	90 00	0	∞	∞
3	a	∞ 0	100	90 00	90 00	90 00	0 00	90 00	0 00	∞	0	∞
4	m	∞	110	55 30	90 00	90 00	90 00	55 30	34 30	1.4548	∞	∞
5	n	∞ 2	120	36 02	90 00	90 00	90 00	36 02	53 58	0.7274	∞	∞
6	k	0 ½	012	0 00	32 12	0 00	32 12	0 00	32 12	0	0.6296	0.6296
7	q	01	011	0 00	51 33	0 00	51 33	0 00	51 33	0	1.2592	1.2592
8	r	02	021	0 00	68 20	0 00	68 20	0 00	68 20	0	2.5184	2.5184
9	o	10	101	90 00	61 22	61 22	0 00	61 22	0 00	1.8319	0	1.8319
10	z	1	111	55 30	65 47	61 22	51 33	48 44	31 06	1.8319	1.2592	2.2229

parallel with the prism face exhibit in convergent polarized light an optic axis emerging at an angle of about 11° with the normal to the plate. The plane of the optic axes is normal to the elongation and parallel with the basal pinacoid (001). The refractive indices were measured by the immersion method under the microscope. The values are listed for sodium light and may be in error by ±0.002.

$$\alpha = 1.514 \quad \beta = 1.546 \quad \gamma = 1.592$$

Optical orientation

$$a = \gamma \quad b = \alpha \quad c = \beta$$

The optic axial angle of a crystal immersed in a liquid of refractive index β was measured directly on an axial angle apparatus and found to be

$$2V_\gamma = 82°10' \text{ for red light } (0.65\mu)$$
$$2V_\gamma = 82°12' \text{ for blue light } (0.48\mu)$$

Dispersion of optic axes slight. Optical character positive.

The foregoing crystallographical and optical data agree very closely with the few data listed by Will and Peters in their original paper. The axial ratios are

$a:b:c = 0.6873:1:1.2600$ Will and Peters
$a:b:c = 0.6874:1:1.2592$ Wright

Observed forms

(110) (011) (012) (001) Will and Peters
(110) (011) (012) (001) (010) (100) (120) (021) (111) (101) Wright

No cleavage observed.

Plane of optic axes is (001).

On a prism face (110) observed in convergent polarized light an optic axis emerges at an angle of 30° (Will and Peters) or 10° (Wright) with the normal to the plate and in the direction of the b axis.

In view of this agreement there is no question that rhamnonic lactone 1,5 is the substance measured crystallographically and optically by Will and Peters.

Rhamnonic Lactone 1,4.—Crystallized from solution in acetone. Crystal system orthorhombic; axial ratio $a:b:c = 0.7772:1:0.3484$. The crystals are prismatic in shape and measure up to 15 mm. in length and 4 mm. in width. In general they are not so clear and well developed as the 1,5-crystals. Only one doubly terminated crystal was observed. In comparison with the wedge-like terminations of the 1,5-crystals, the 1,4-crystals are bluntly terminated by the forms (011), (101) and (111). The prism (120) dominates the prism zone with (110) and (010) subordinate in character; the form (120) might have been chosen as unit prism; but by so doing the dome and pyramid faces would have had larger indices and this would not be advantageous. The shape of the crystals is illustrated in Figs. 3 and 4.

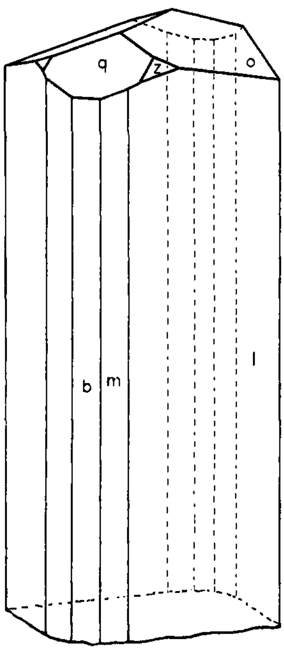

Fig. 3.—Crystal of rhamnonic lactone-1,4.

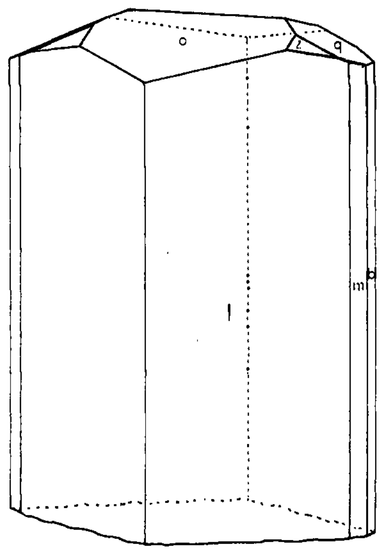

Fig. 4.—Crystal of rhamnonic lactone-1,4 showing the *b* axis pointing toward the observer. Crystal turned at 90° to the position shown in Fig. 3.

In Fig. 4 the crystal is shown turned at 90° to its position in Fig. 3, and gives its appearance had the prism (120) been selected as unit prism.

The crystals occur in irregular clusters and groups. Etch figures were not observed. Many of the crystal faces are poorly developed and irregular and show crystal growth phenomena; these are not favorable to the production of clear-cut etch figures. No cleavage was observed; the fracture is conchoidal.

Five small crystals of the 1,4-substance were measured on the goniometer. The faces on the larger crystals gave multiple signals and were useless for goniometric work. In the prism zone the angle between the faces 120:$\bar{1}$20 averages 65°30′; angle 110:1$\bar{1}$0 = 75°42′ (mean of 11 interfacial angles); the average polar distance for (011) is 19°13′ (mean of 10 values ranging from 19°09′ to 19°20′) for (101) the polar angle ρ = 24°09′ (average of 7 values ranging from 24°00′ to 24°13′). The unit pyramid faces are small and on no single crystal were more than two faces of the complete form observed. In the development of the crystal faces there is a noticeable lack of symmetry; this may indicate a class other than the holohedral class of the orthorhombic system.

In Table II are listed the angles and data for the several observed forms as computed from the axial ratios deduced by the usual methods from the averages of the best measured angles.

Table II

Rhamnonic Lactone 1,4

$a = 0.7772$ $\quad a_0 = 2.2308$ $\quad p_0 = 0.4483$

$c = 0.3484$ $\quad b_0 = 2.8703$ $\quad q_0 = 0.3484$

No.	Letter	Symb.	Miller	φ	ρ	ξ_0	η_0	ξ	η	x Prisms $x:y$	y	d
1	b	0 ∞	010	0°00′	90°00′	0°00′	90°00′	0°00′	90°00′	0	∞	∞
2	m	∞	110	52 09	90 00	90 00	90 00	52 09	37 51	1.2867	∞	∞
3	l	∞ 2	120	32 45	90 00	90 00	90 00	32 45	57 15	0.6434	∞	∞
4	o	01	011	0 00	19 13	0 00	19 13	0 00	19 13	0	0.3484	0.3484
5	q	10	101	90 00	24 09	90 00	24 09	90 00	24 09	0.4483	0	0.4483
6	z	1	111	52 09	29 35	24 09	19 13	22 57	17 38	0.4483	0.3484	0.5678

The refractive indices were measured by the immersion method. The values are given for sodium light and may be in error ±0.002. The principal refractive indices are

$$\alpha = 1.497 \quad \beta = 1.525 \quad \gamma = 1.532$$

Optical orientation

$$a = \gamma \quad b = \beta \quad c = \alpha$$

The plane of the optic axes is parallel with the elongation of the crystal. Optical character negative; optic axial angle small. The optic axial angle was measured directly both under the microscope and on an axial angle apparatus:

$$2E_\alpha = 80°44' \text{ for red light } (0.65\mu)$$
$$2E_\alpha = 76°30' \text{ for blue light } (0.48\mu)$$

The dispersion of the optic axes is large and much greater than in the 1,5-crystals, in which it is hardly perceptible. Extinction is parallel and negative. Plane of the optic axes is the brachy-pinacoid (010).

These crystallographical and optical data prove conclusively that rhamnonic lactone 1,4 is quite different from rhamnonic lactone 1,5. The two substances are most easily distinguished under the microscope. All of the optical constants are so different that even in very fine grains the determination should be easy.

Summary

The crystallographical and optical properties of the 1,4- and 1,5-lactones of rhamnonic acid have been measured. The results show conclusively

that the *l*-rhamnonic lactone which Will and Peters measured in 1889 was the 1,5- rather than the 1,4-lactone.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

PREPARATION AND BACTERIOLOGICAL ACTION TOWARD B. LEPRAE OF CERTAIN OLEFINIC ACIDS. XVII[1]

BY E. BROWNING, H. W. WOODROW AND ROGER ADAMS

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Although the various cyclopentenyl alkyl acetic acids showed only slightly greater bactericidal action to *B. Leprae* than the corresponding cyclopentyl acids, a more careful study of the effects of an olefin linkage substituted in various dialkyl acetic acids has been undertaken. Representatives of three types of acids were prepared, allyl alkyl acetic acids, undecenyl alkyl acetic acids, and certain dialkyl acetic acids with the olefin linkage in the α,β-position. The bacteriological results are shown in Table I. The authors are indebted to Dr. W. M. Stanley for making these tests.

TABLE I

BACTERIOLOGICAL ACTION TOWARD *B. Leprae*

	Dilutions of sodium salts in thousands												
	5	15	25	50	62	74	85	100	125	155	192	250	330
Allyl alkyl acetic acids													
$C_3H_5CH(CO_2H)C_9H_{19}$-*n*	−	−	−	−	−	−	+	+	+	+	+	+	+
$C_3H_5CH(CO_2H)C_{10}H_{21}$-*n*	−	−	−	−	−	−	−	±	+	+	+	+	+
$C_3H_5CH(CO_2H)C_{11}H_{23}$-*n*	−	−	−	−	−	−	−	−	−	+	±	+	+
$C_3H_5CH(CO_2H)C_{12}H_{25}$-*n*	−	−	−	−	−	−	−	−	−	−	−	−	+
$C_3H_5CH(CO_2H)C_{13}H_{27}$-*n*	−	−	−	−	−	−	−	−	−	±	+	+	+
$C_3H_5CH(CO_2H)C_{14}H_{29}$-*n*	−	−	−	−	−	−	−	−	+	+	+	+	+
Undecenyl alkyl acetic acids													
$C_{11}H_{21}CH(CO_2H)C_4H_9$-*n*	−	−	−	−	−	−	−	−	−	−	−	+	+
$C_{11}H_{21}CH(CO_2H)C_5H_{11}$-*n*	−	−	−	−	−	−	±	±	±	−	±	±	+
$C_{11}H_{21}CH(CO_2H)C_6H_{13}$-*n*	−	−	−	−	±	±	±	+	+	+	±	+	+
$C_{11}H_{21}CH(CO_2H)C_7H_{15}$-*n*	−	−	−	±	+	±	±	+	+	+	+	+	+
α,β-Unsaturated acids													
$C_3H_7CH{=}C(CO_2H)C_4H_9$-*n*	−	+	+	+	+	+	+	+	+	+	+	+	+
$C_6H_{13}CH{=}C(CO_2H)C_7H_{15}$-*n*	−	−	−	−	−	−	−	−	−	−	−	±	+
$C_7H_{15}CH{=}C(CO_2H)C_8H_{17}$-*n*	−	−	−	−	−	−	−	−	−	−	+	+	+

By comparison of these data with those of the corresponding saturated acids containing the same number of carbon atoms[1b] it can be concluded that the presence of the olefin linkage has very little effect, if any, upon the bactericidal action. Moreover, the position of the olefin linkage in relation to the carboxyl appears to have no definite significance.

[1] The previous two papers in this series are (a) Ford and Adams, XVI, THIS JOURNAL, **52,** 1259 (1930); (b) Stanley, Jay and Adams, XV, *ibid.*, **51,** 1261 (1929).