

29. The Crystal Form of Anhydrous Citric Acid.

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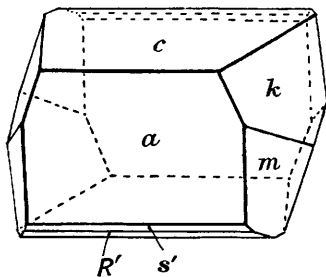
It has long been known that, in addition to the familiar monohydrate of citric acid, which crystallises in the orthorhombic system (Groth, "Chemische Kristallographie," iii, p. 475), the acid may be obtained anhydrous by cooling its hot concentrated aqueous solutions (Buchner and Witter, *Ber.*, 1892, **25**, 1159; Meyer, *Ber.*, 1903, **36**, 3599). As no crystallographic description of this substance has been recorded, we have now examined it goniometrically. Suitable crystals were obtained with considerable difficulty.

Anhydrous citric acid crystallises in the holohedral class of the monoclinic system with axial angle $\beta = 99^\circ 7'$ and axial ratios $a : b : c = 1.936 : 1 : 1.150$. Barker classification angles: $a(100) : m(110) = 62^\circ 23'$, $c(001) : r(101) = 29^\circ 25'$, $r(101) : a(100) = 51^\circ 28'$, and $b(010) : q(011) = 41^\circ 23'$. The following is a list of the forms observed and the mean angular measurements obtained with a two-circle goniometer from five selected crystals:

	$a(100)$.	$c(001)$.	$R(\bar{1}01)$.	$s(\bar{2}01)$.	$m(110)$	$k(121)$
ρ	$90^\circ 0'$	$90^\circ 0'$	$90^\circ 0'$	$90^\circ 0'$	$*27^\circ 37'$	$*29^\circ 4'$
ϕ	$0^\circ 0'$	$*80^\circ 53'$	$111^\circ 5'$	$134^\circ 5'$	$0^\circ 27'$	$*51^\circ 28'$

The usual habit of the crystals is as shown in the annexed figure with R and s small, the latter being sometimes absent.

The substance has a low positive double refraction. In convergent polarised light, one optic axis is seen emerging nearly perpendicular to the face a , and the second through the face R , the optic axial plane being parallel to the plane (010).



The density of the crystals, found by flotation in a mixture of acetylene tetrabromide and light petroleum, is $d_4^{18^\circ}(\text{vac.}) = 1.665$, and the m. p. $156-157^\circ$ (corr.).

In view of the discussion which formerly arose as to the conditions under which the anhydrous and the hydrated form may be deposited from solution (*loc. cit.*), we have now determined the transition point. Observations were made of the cooling curve of pure citric acid (thrice recrystallised from distilled water) in the presence of water.

The apparent temperature of arrest was somewhat sensitive to variations in the temperature of the bath surrounding the air jacket—presumably owing to a low value of the heat of transformation. Care was therefore taken to keep the outer bath as near to the observed temperature as possible, and the temperature of arrest was taken both during heating and cooling. Found: with falling temperature 36.15° ; with rising temperature 36.45° ; mean value 36.3° . The thermometer, graduated in 0.1° , was checked by observing the transition point of sodium sulphate decahydrate (Found: 32.4° ; Richards and Wells, *Z. physikal. Chem.*, 1903, **43**, 465, give 32.38°).