

Chemistry. — “Two Isomeric Chloro-Tetracetyl-d-Fructoses”. By Prof. F. M. JAEGER.

(Communicated at the meeting of June 26, 1920).

§ 1. Some time ago Dr. D. H. BRAUNS observed that, when phosphorus pentachloride at low temperatures acts upon β -tetracetyl-fructose dissolved in dry chloroform, under differently chosen circumstances, two compounds are formed in the reaction, which both have the composition of a chloro-tetracetyl-fructose, but which differ considerably in properties. The one isomeride: α -chloro-tetracetyl-d-fructose, melts at 83° C., and has a specific rotation of $[\alpha]_D^{20} = -160^{\circ},9$ (the maximum value measured in chloroform-solution); it is produced only, if aluminiumchloride be added to the reaction-mixture as a catalyst. Contradictory to what one might perhaps expect beforehand from this mode of preparation, this α -derivative appears to be unstable to such a degree, that it is decomposed into an impure β -tetracetyl-fructose and an acid liquid within twenty-four hours, if exposed to the air at room-temperature. Only if preserved in the dark in an ice-box at a temperature of 0° C., it appeared possible to recrystallize the substance repeatedly from dry ether, if moisture be excluded as carefully as possible; even then, however, the decomposition mentioned above finally sets in. On the other hand, the other isomeride: β -chloro-tetracetyl-d-fructose, which is produced under the same circumstances, if only no catalyst be added to the mixture, appears to be a very stable substance in comparison with the labile α -derivative, and may be recrystallized from most of the organic solvents, without being changed to any appreciable degree. It melts at 108° C., and has, in chloroform-solution, a specific rotation of $[\alpha]_D^{20} = +45^{\circ},2$. While the α -compound has an intensely bitter taste, the β -derivative tastes only feebly bitter, and it is considerably more soluble in most solvents than the α -isomeride. The β -compound is also not absolutely stable: when repeatedly recrystallized from absolute alcohol, the formation of ethylacetate can be observed; and when solutions in commercial benzine are slowly evaporated at 18° C., the crystals obtained appear to be slightly coloured pink, while the mother-liquid also assumes a gradually increasing violet or even brown colour. In comparison with the α -compound, however, it can be considered to be “stable”; as far as known, these two

isomerides cannot be transformed directly into each other. A 0,1 normal solution of $NaOH$ causes all the chlorine to be split-off from the α -derivative within five hours at 0° C.; the β -derivative, however, does not liberate its chlorine under the same circumstances. The determinations of carbon, hydrogen, and chlorine (Carius), and those of the molecular weight, gave with both substances the same results, all agreeing with the composition of a chlorotetracetyl-fructose: $C_8H_7O(C_2H_3O_2)_4Cl$.

§ 2. In connection with the measurements of the isomeric α - and β -pentacetyl-¹⁾, and tetracetyl-d-fructoses²⁾ formerly made by the author, it appeared of interest to study these two isomerides also from a crystallographical point of view, and to compare them with each other, as well as with the derivatives mentioned above. Chiefly with respect to the instability of the α -derivative, it was necessary, therefore, to prepare both isomeric substances once more, and immediately to measure the crystals eventually obtainable under favourable circumstances. This was possible to me by Mr. BRAUN's kind assistance, who placed a quantity of the β -tetracetyl-derivative already described at my disposal, as well as his notes about the method of preparation of the chloro-derivatives. I wish to express to him also here my sincere thanks for his interest and help.

The preparation, especially of the α -compound, must be carefully supervised; it is not so easy as it might perhaps appear to be. More particularly, the tetracetyl-fructose used must be free from acid, and the reagents applied may not contain moisture, nor may appreciable changes of temperature occur during the reaction. It is desirable to work very rapidly: therefore, the evaporation of the solutions must take place under a glass bell-jar connected with a drying apparatus by blowing over the surfaces air carefully dried with calciumchloride. The α -compound can best be recrystallized from dry ether in the ice-box at 0° C., and in darkness, moisture being carefully excluded. The same precautions should be taken in preparing the β -isomeride; but the substance may be recrystallized in the usual way at roomtemperature. Purification of the β -compound can best be done by recrystallizing it from boiling absolute alcohol; to obtain beautiful and measurable crystals, the substance is dissolved in pure benzene, or in a mixture of chloroform and benzene, from which it is deposited on slow evaporation in big, transparent, prismatic

¹⁾ F. M. JAEGER. Proceed. R. Acad. of Sciences, Amsterdam, 20, 280, (1918).

²⁾ F. M. JAEGER. Proceed. R. Acad. of Sciences, Amsterdam, 10, 563, (1908); Zeits. f. Kryst. und Miner., 45, 539, (1908).

crystals, possessing about the same refractive index as the remaining mother-liquor, and, therefore, being almost invisible in it.

Preparation of α -Chloro-tetracetyl-d-Fructose.

30 Grams of freshly recrystallized and carefully dried β -tetracetylfructose are dissolved in 90 ccm. dry chloroform in a glass bottle with ground stopper; the solution is cooled to 0° C. by means of ice. Now first 7.5 grams of finely powdered, dry Al_2Cl_6 is added, and afterwards 19 grams of dry phosphoruspentachloride. When all is at 0° C., the vessel is removed from the ice-bath, and the mixture is left at room-temperature for 30 minutes, while it is stirred from time to time and while an opportunity is given to the vapours of the hydrochloric acid formed and to those of the chloroform to escape. Then the bottle is placed once more into the ice, the contents of it, after being cooled rapidly, brought into a separating funnel, and the liquor rapidly washed with a solution of sodium-bicarbonate cooled with pieces of ice; finally it is again washed with some ice-water. The chloroform-solution is subsequently dried by means of coarsely grained anhydrous $CaCl_2$, and the dry solution, after being filtered, rapidly evaporated in a wide crystallisation-dish by means of a strong current of dry air, under a glass bell connected with drying apparatus. The very viscous mother-liquor gets finally crystallized; crusts of solid matter are deposited, which are put upon a hard filter, rapidly sucked-off, the crystals pressed between sheets of filterpaper, and dissolved in dry ether. In the ice-box colourless needles or thicker prisms were gradually deposited from the solution, which, if suited for measurements, must be investigated immediately. All necessary precautions being taken, the reaction yields about 60–65% of the theoretical quantity.

Preparation of β -chloro-tetracetyl-d-fructose. The preparation of this isomeride occurs just in the same way as that of the α -derivative, only no Al_2Cl_6 being added to the solution. After the chloroform has been evaporated, a small quantity of absolute alcohol is added, by which immediately an aggregation of colourless needles is formed, which is treated as described above and then repeatedly recrystallized from boiling absolute alcohol. Measurable crystals are best obtained from benzene; the substance crystallizes in short, thick prisms, the α -isomeride (from ether) in more tiny, colourless needles. In both cases a yield of about the same percentage may be obtained.

§ 3. α -Chloro-tetracetyl-d-fructose (mpt. 83° C.) crystallizes from dry ether at 0° C. in the shape of small colourless and transparent needles, the end-faces of which are often only rudimentarily developed.

They are rhombic, most probably bisphenoidal, with the parameters: $a : b : c = 0,9759 : 1 : 0,3284$.

Forms observed: $a = \{100\}$, narrow, but broader than $b = \{010\}$, which form generally is present only with a single, extremely narrow plane; $m = \{110\}$, large and lustrous, commonly yielding multiple reflexes; $r = \{101\}$, giving sharp mirror-images. In the z one

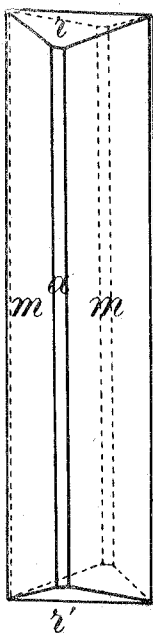


Fig. 1.

α -Chlorotetra-
acetyl-d-fructose.

of the c -axis the angular values are mostly oscillating, the reflexes being multiple; with very thin individuals, however, exact measurements could be made. The aspect of the crystals is that of prisms elongated in the direction of the c -axis. No distinct cleavage was found. The prism-faces (110) and $(\bar{1}\bar{1}0)$ were much more lustrous and yielded much sharper images than the faces $(\bar{1}10)$ and $(1\bar{1}0)$, which ordinarily were somewhat curved and duller.

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) = *$	44 18	—
$r : r = (101) : (\bar{1}01) = *$	37 12	—
$m : b = (110) : (010) =$	45 44	$45^\circ 42'$
$m : m = (110) : (\bar{1}10) =$	91 28	91 24
$a : r = (100) : (101) =$	71 24	71 24
$r : m = (101) : (110) =$	77 10	$76 18\frac{2}{3}$
$r : m = (101) : (\bar{1}10) =$	77 2	$76 18\frac{2}{3}$

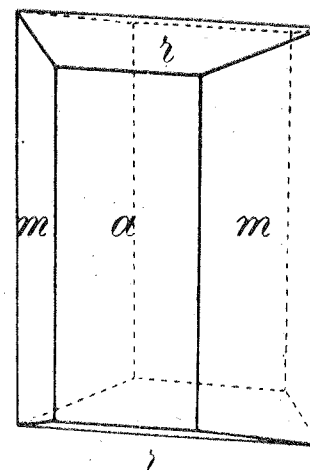


Fig 2 β -Chloro-tetracetyl-
d-Fructose.

Big, colourless crystals, yielding, however, ordinarily multiple reflections, and imperfectly built.

Rhombic-bisphenoidal.

$$a : b : c = 1,7478 : 1 : 0,7112.$$

Forms observed: $a = \{100\}$ and $m = \{110\}$, well developed and giving sharp images; $r = \{101\}$, large, eminently reflecting; once a positive bisphenoid, probably $\{523\}$, and very subordinate, was observed, difficultly measurable.

The crystals are positively birefringent. The optical axial plane is $\{001\}$; on the prism-faces, just at the border of the field, the emergence of an optical axis is observable. The dispersion has a rhombic character, with $\rho > v$. The aspect of the crystals is very much like that of the β -derivative.

§ 4. β -Chloro-tetracetyl-d-fructose (mpt. 108° C.) crystallizes from benzene in the shape of large, clear, very lustrous and short prismatic crystals, which with exception of their smaller development in the direction of the c -axis, show an undeniable analogy with the crystals of the α -compound.

The aspect is short prismatic in the direction of the *c*-axis, occasionally also isometrically developed.

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) = *$	$60^{\circ} 13\frac{1}{2}'$	—
$a : r = (110) : (101) = *$	$67 51\frac{1}{2}'$	—
$m : m = (110) : (\bar{1}10) =$	$59 33$	$59^{\circ} 33'$
$r : r = (101) : (\bar{1}01) =$	$44 17$	$44 17$
$r : m = (101) : (110) =$	$79 10$	$79 12\frac{3}{4}$
$o : m = (523) : (110) = \text{ca.}$	$50 56$	$51 51$
$o : o = (523) : (\bar{5}23) = \text{ca.}$	$48 50$	$49 12\frac{1}{2}$
$o : o = (523) : (5\bar{2}3) =$	$117 30$	$117 0$

No distinct cleavage was observed.

§ 5. There is evidently no distinct form-analogy present between the two isomeric *chloro-tetracetyl-d-fructoses*, in contradiction to what was formerly stated in the case of both α - and β -*pentacetyl-d-fructoses*. The substitution of a Cl-atom for hydrogen, has evidently, however, not a lowering of the degree of symmetry of the original substances as a consequence, all four acetyl-derivatives being *rhombic-bisphenoidal*. However, from the results obtained, it appears still to be impossible to demonstrate a more intimate analogy of the crystal-forms of the α - and β -derivatives of this series and that studied formerly.

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Chemistry. — “On the Crystalforms of some Substituted Amides of *Para-Toluenesulphonic Acid*.” By Prof. F. M. JAEGER.

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§ 1. In the following the results are communicated of an investigation concerning the crystallographical properties of a series of substituted *amides* derived from *p-toluene-sulphonic acid*¹⁾, already prepared by Prof. VAN ROMBURGH in 1902. These preparations, which in general occur in beautiful crystals, were ceded to me a long time ago by the said chemist for the purpose indicated; but the results of these measurements have not been published hitherto.

To colleague VAN ROMBURGH's benevolence I am indebted also for some still lacking data on the specific weight of several of these substances.

In the text occasionally attention has been drawn to some regularities of the crystalforms of these derivatives, which, from a chemical standpoint, are closely related to each other; a review of the numerical data is, moreover, added to this paper at the end. Distinct relations in the crystalforms of these derivatives have, however, not been found in great number, notwithstanding their close chemical relationship.

§ 2. I. Nitro-*p*-Toluene-sulpho-amide.

This substance, which melts at 141° C., crystallizes from ethyl-alcohol in big, very transparent crystals, which often possess curved

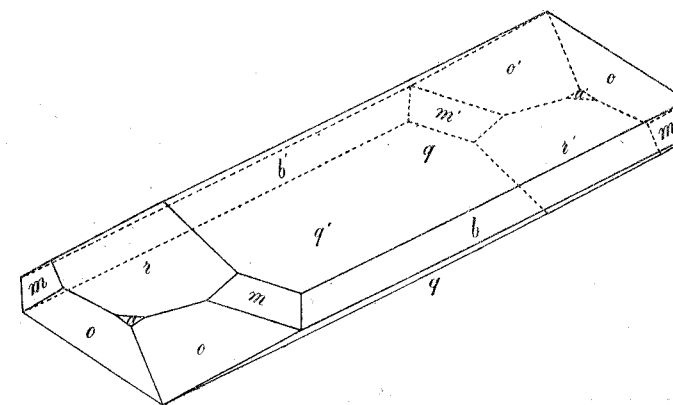


Fig. 1. Nitro-*p*-Toluene-sulpho-amide.

¹⁾ Cf. also: P. VAN ROMBURGH, *Proceed. Acad. of Sciences Amsterdam*, Februari, (1902).