TABLE I

Solvents from which the compounds were crystallized: A, alcohol; B, glacial acetic acid; C, butanol; D, mixture of alcohol and dioxane; E, water.

No.	Compound	Yield, %	Cryst. from	M. p., °C.[a]	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
1	N-2-Nitrophenylbenzenesulfonamide	70	A	102.2–102.5[b]	$C_{12}H_{10}N_2O_4S$				
2	N-Sodium salt of 1	81		239–240[c]	$C_{12}H_9N_2NaO_4S$				
3	N-2-Nitrophenyldibenzenesulfonamide	72	B, C or D	189.8–190.5	$C_{18}H_{14}N_2O_6S_2$	6.70	6.54	15.31	15.16
4	N-2-Aminophenylbenzenesulfonamide	64	50% A	169.3–170.0[d]	$C_{12}H_{12}N_2O_2S$				
5	N,N′-(*o*-Phenylene)-bis-benzenesulfonamide	71	B	190.3–190.8[e]	$C_{18}H_{16}N_2O_4S_2$				
6	N-2-Aminophenyldibenzenesulfonamide	41–62	A	149.5–149.9	$C_{18}H_{16}N_2O_4S_2$	7.22	7.23	16.52	16.23
7	N-2-Benzenesulfonylaminophenyldibenzenesulfonamide	83	A or B	157.1–157.3[f]	$C_{24}H_{20}N_2O_6S_3$	5.30	5.30	18.20	18.02
8	Benzenesulfonic acid salt of 4	29[g]	A or E	204.9–205.4	$C_{18}H_{18}N_2O_5S_2$	6.90	6.70	15.76	15.46
9	N,N′-Disodium salt of 5	90		Not below 275	$C_{18}H_{14}N_2Na_2O_4S_2$	6.48	6.17	14.81	14.17

[a] All melting points were taken with completely immersed short stem thermometers calibrated by the National Bureau of Standards and have been corrected. [b] Lellmann[1] reported 104°; Morgan and Micklewait,[2] 104°; Opolski, 102–103.5°. [c] Opolski[3] reported 230° (our sample shrank a little at 230°). [d] Lellmann[1] reported 168°; Morgan and Micklewait,[2] 165–167°. [e] Hinsberg and Strupler[4] reported 186°. [f] This is believed by us to be the same compound that Hinsberg and Strupler[4] reported as the tetrabenzenesulfonyl derivative with a melting point of 150–151°. [g] As a by-product in the preparation of compound number 5 by the method of Hinsberg and Strupler.

was difficult even with mechanical stirring and the yield was often very low. N-2-Benzenesulfonylaminophenyldibenzenesulfonamide was prepared by heating on a water-bath for fifty hours a solution of 25 g. of the N,N′-disodium salt of N,N′-(*o*-phenylene)-bis-benzene-sulfonamide and 10.2 g. of benzenesulfonyl chloride in 250 cc. of dioxane. The compound was obtained by evaporating the solution to dryness, washing with water and crystallizing the residue from glacial acetic acid. The disodium salt of N,N′-(*o*-phenylene)-bis-benzenesulfonamide was prepared by dissolving the amide in a hot solution of sodium hydroxide (2 cc. of 10% sodium hydroxide for each gram of the amide). The product crystallized when the solution was cooled and was then filtered, washed with a very little ice cold water and then with alcohol. The compound was dried on porous tiles and then at 120° for one hour.

Data for these compounds are listed in the table. The author is indebted to Miss Victoria N. Bodrasky for some of the analytical data.

Summary

1. All but one of the N-substituted benzenesulfonyl derivatives of *o*-nitroaniline and *o*-phenylenediamine have been prepared. Improvements have been made in the methods of preparation of some of those previously reported.

2. The substance described in the literature as the tetrabenzenesulfonyl derivative of *o*-phenylenediamine[4] is probably the tribenzenesulfonyl derivative. Our attempts to prepare the tetra derivative have been unsuccessful.

STORRS, CONN. RECEIVED MAY 17, 1937

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies in the Ketone Sugar Series. VIII. The Structure of *l*-Sorbose Pentaacetate

BY FRANCIS B. CRAMER AND EUGENE PACSU

It has been shown by Arragon[1] that a solution of zinc chloride in acetic anhydride acts upon *l*-sorbose to form, under varying conditions, a tetraacetate and a pentaacetate. Arragon later[2] reported that a much better yield of tetraacetate was obtained by the action of acetic anhydride and pyridine on sorbose.

Schlubach and Vorwerk[3] were able to prepare the pentaacetate, using zinc chloride as catalyst, in greatly improved yield by a modification of the conditions. These authors found pentaacetylsorbose to be strikingly indifferent to halogenating agents. As this behavior is characteristic of the pentaacetylfructose which Pacsu and Rich[4] have shown to have open chain structure, Schlubach and Vorwerk expressed the belief that they were dealing with pentaacetyl-keto-sorbose.

---

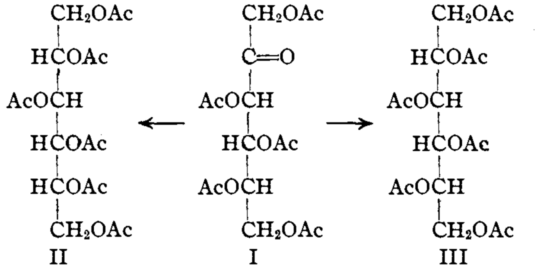
[1] Arragon, *Compt. rend.*, **196**, 1733 (1933).

[2] Arragon, *ibid.*, **198**, 1508 (1934).

[3] Schlubach and Vorwerk, *Ber.*, **66**, 1251 (1933).

[4] Pacsu and Rich, THIS JOURNAL, **55**, 3018 (1933).

This conclusion has now been proved definitely, as in the case of open chain fructose and turanose acetates, by catalytic reduction.[4] When glacial acetic acid was used as solvent the reduction was sluggish and incomplete. However, finely powdered sorbose pentaacetate (I) suspended in absolute ether, when shaken two and one-half hours with platinum catalyst and hydrogen under four atmospheres' absolute pressure, went into solution and lost its ability to reduce Fehling's solution. Upon working up the reaction mixture and subsequent acetylation of the resulting sirup, crystalline hexaacetyl-*d*-sorbitol[5] (II) and hexaacetyl-*l*-iditol (III) were obtained in good yield.



II I III

These substances were separated easily by crystallization from ether and from alcohol and identified by their melting points and specific rotations. It becomes necessary, therefore, to designate the only crystalline pentaacetate of sorbose as pentaacetyl-keto-sorbose.

As in the case of pentaacetyl-keto-fructose and octaacetyl-keto-turanose, the sorbose acetate would not form derivatives with such typical ketone reagents as *p*-nitrophenylhydrazine and semicarbazide. A colorless acetone solution of the sorbose acetate becomes deeply yellow on the addition of a few drops of dilute sodium hydroxide solution. After neutralization with dilute sulfuric acid, the color disappears and the solution will reduce potassium permanganate dissolved in acetone. This peculiar behavior has been reported by Pacsu and Rich[4] as characteristic of the keto derivatives of fructose and turanose.

Regarding the preparation of pentaacetyl-keto-sorbose, it was found that this substance could be prepared by the acetylation of tetraacetylsorbose with acetic anhydride and zinc chloride either at room temperature or at 50°. The yield of this reaction was quite satisfactory, but the comparatively low yields obtained in the preparation of the tetraacetate made the method impractical. The use of Schlubach's procedure[3] is more advantageous for preparative purposes.

Arragon has reported that tetraacetylsorbose, prepared by the action of zinc chloride and acetic anhydride, when crystallized from ether, contained ether of crystallization and melted at 65°. It was also stated that this product lost 5% of its weight on heating to 30° *in vacuo*, and that the melting point then became 96°. In the course of the present investigation it has not been possible to confirm these observations. Tetraacetylsorbose, prepared strictly according to the method of Arragon and recrystallized from ether at 0°, showed the melting point 100–101.5° immediately after removal from the mother liquor and did not change either in weight or melting point on heating at 80° *in vacuo* for one hour.

Arragon later[2] reported a difference in rotations and melting points between the tetraacetylsorbose prepared with zinc chloride as catalyst and that made by using pyridine and acetic anhydride. These observations, likewise, could not be confirmed. Samples prepared by each method, after repeated recrystallization from absolute ether, showed melting points and mixed melting point of 100–101.5° and specific rotation[6] −19.4°. It appears, therefore, that at present there exist only two crystalline acetates of sorbose: tetraacetylsorbose, and pentaacetyl-keto-sorbose.

In the reduction of sorbose pentaacetate, of the mixture of acetylated alcohols obtained 60% was the *l*-iditol derivative. This may be saponified easily to the free alcohol. Since the two halves of the *l*-iditol molecule are identical in structure and configuration, it is to be anticipated that controlled oxidation will give a good yield of *l*-idonic acid, the lactone of which may be reduced to *l*-idose.[7] The preparation of this rare and little known sugar by the method outlined will be undertaken in the near future.

Acknowledgment is made to Merck and Company, Incorporated, Rahway, New Jersey, for the sorbose used in this investigation.

---

(5) The sorbitol obtained by the reduction of *l*-sorbose might logically be called *l*-sorbitol. However, the compound was first prepared by the reduction of *d*-glucose [Meunier, *Compt. rend.*, **111**, 49 (1890)] and *d*-fructose [Fischer, *Ber.*, **23**, 3684 (1890)] and is usually referred to as *d*-sorbitol (Tollens and Elsner, "Kurzes Handbuch der Kohlenhydrate," Johann Ambrosius Barth, Leipzig, 1935, p. 275). In at least one case, the substance has been designated as *l*-sorbitol [Sah, *Ber.*, **70**, 498 (1937)]. It appears desirable to retain the older nomenclature to avoid confusion in the literature.

(6) All specific rotations recorded in this paper were measured at 20° using light of the wave length of the sodium D lines, and chloroform as solvent.

(7) Fischer and Fay, *Ber.*, **28**, 1975 (1895).

Experimental Part

Reduction of Pentaacetyl-keto-sorbose.—Five grams of powdered pentaacetyl-keto-sorbose, prepared according to the procedure of Schlubach and Vorwerk,[3] and 0.2 g. of platinum catalyst[8] were suspended in 300 cc. of absolute ether and shaken with hydrogen under four atmospheres' absolute pressure for two and one-half hours. During this time all of the pentaacetate dissolved and the material in solution was devoid of action toward boiling Fehling's solution. The ether solution was filtered free of platinum and evaporated to a sirup *in vacuo*. The residue was dissolved in 40 cc. of acetic anhydride containing 0.5 g. of fused zinc chloride, and the solution was kept at 50° for one and one-half hours. After cooling, this was stirred for one hour with an equal volume of cold water and poured into an excess of saturated sodium bicarbonate solution, whereupon the acetylated alcohols separated as a white powder. The whole was extracted several times with chloroform, the extracts united, dried with calcium chloride, filtered, and evaporated *in vacuo* to a semicrystalline mass. This was dissolved in 300 cc. of boiling ether. On cooling to room temperature, 1.9 g. of large hexagonal plates separated. Concentration of the solution brought the total yield of pure hexaacetyl-*l*-iditol[9] to 3.1 g.; m. p. 121.5° and specific rotation −25.5°. The mother liquor was evaporated *in vacuo* to a sticky mass. This was taken up in *ca.* 10 cc. of hot alcohol and placed in the ice box where 1.9 g. of hexaacetyl-*d*-sorbitol[4] separated. After one recrystallization from alcohol the substance showed the correct m. p. of 99° and specific rotation 10°.

Acetylation of Tetraacetylsorbose.—Two grams of sorbose tetraacetate was dissolved in 10 cc. of distilled acetic anhydride containing 0.1 g. of fused zinc chloride, and the mixture was kept at 50° for one hour. After cooling, the solution was stirred with 10 cc. of cold water for one and one-half hours and poured into an excess of saturated sodium bicarbonate solution. The whole was extracted three times with chloroform, the extracts combined, dried with calcium chloride, filtered, and evaporated to dryness *in vacuo*. The residue was dissolved in a little hot alcohol and placed in the ice box. The solution deposited 1.5 g. of crystalline material which was identified as pentaacetyl-keto-sorbose by its melting point and mixed melting point.

In another experiment, 0.5 g. of tetraacetylsorbose was dissolved in 10 cc. of acetic anhydride containing 0.1 g. of fused zinc chloride and left at room temperature for one day. On working up the mixture as above, 0.3 g. of pentaacetyl-keto-sorbose was obtained.

Summary

l-Sorbose pentaacetate is a derivative of the open chain sorbose since, on reduction and subsequent acetylation, crystalline hexaacetyl-*d*-sorbitol and hexaacetyl-*l*-iditol are obtained.

Pentaacetyl-keto-sorbose may be prepared by the acetylation of tetraacetylsorbose with acetic anhydride and fused zinc chloride.

Observations, reported in the literature, concerning certain properties of tetraacetylsorbose cannot be confirmed.

Princeton, N. J.

Received June 7, 1937

---

(8) Adams, Vorhees and Shriner, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 92.

(9) Bertrand, *Bull. soc. chim.*, [3] **33**, 1073 (1906).

[Contribution from the Pathological Division, Bureau of Animal Industry]

Lupine Studies. XII. The Alkaloids of *Lupinus laxus* Rydb.

By James Fitton Couch

Lupinus laxus was originally reported from Wyoming and Montana by Rydberg[1] as a new species closely related to *L. laxiflorus*. The material used in the present study was collected at Fish Lake in south central Utah in 1932 and 1934. The first lot was identified by C. P. Smith as *L. laxus* who, however, named specimens of the second collection *L. leucopsis* var. ined. An inquiry addressed to Doctor Smith whether these two names are considered synonymous has remained unanswered. We, therefore, are using the published name in preference to the second identification.

Chemical examination has revealed the presence of four alkaloids in this plant, sparteine, *d*-lupanine, trilupine and a base isomeric but not identical with hydroxylupanine isolated from *L. polyphyllus* by Bergh.[2] The fourth base melts at nearly the same temperature as anhydrous hydroxylupanine but differs in that it does not crystallize with water as does Bergh's alkaloid and the optical rotation is twice as large. The quantity obtained from the plant was too small to permit a thorough investigation and the substance is only provisionally accepted as a new alkaloid pending further study.

The isolation, from this species, of trilupine which was first found in *L. barbiger*[3] is of interest in that it is here associated with *d*-lupanine of which it is the diamino oxide while no *d*-lupanine could be detected in *L. barbiger*. It was found

---

(1) P. A. Rydberg, *Bul. Torr. Club*, 258, 1903.

(2) G. F. Bergh, *Arch. Pharm.*, **242**, 416–440 (1904).

(3) J. F. Couch, This Journal, **58**, 1926 (1936).