

the relationship of the ketose to the two aldoses, we prefer the name *allulose* proposed by Professor William Lloyd Evans.

From commercial distillery residues we have now obtained *d*-allulose by way of its diacetone derivative. This compound when heated with dilute acetic acid decomposes to form the free sugar. The sirup thus prepared was dissolved in water and read in a saccharimeter.

$$[\alpha]^{20}_D = \frac{+0.05^\circ S \times 100}{1.2044 \times 0.5} \times 0.3462 = +2.9^\circ$$

Steiger and Reichstein<sup>2</sup> reported  $[\alpha]^{20}_D +3.1^\circ$ .

Methylation of the crude allulose concentrate followed by a high-vacuum distillation of the product yielded 1,3,4,6-tetramethyl ( $\alpha \rightleftharpoons \beta$ ) methyl *d*-alluloside which distilled as a thick oil from a bath temperature of 105–140° at a pressure of  $8 \times 10^{-5}$  mm.

*Anal.* Calcd. for  $C_{11}H_{22}O_6$ : C, 52.77; H, 8.86;  $OCH_3$ , 62.00. Found: C, 53.00; H, 9.24;  $OCH_3$ , 59.70;  $n^{21.5}_D$  1.4572.

When 0.3199 g. of the tetramethyl methyl alluloside was dissolved in 25 ml. of methyl alcohol containing four drops of concentrated hydrochloric acid and heated in a pressure bottle for two hours at 100°, the product (probably an equilibrium mixture of tetramethyl methyl allulosides) had a specific rotation in sodium light of +36° at 20°.

Further work with allulose derivatives is in progress.

(2) Steiger and Reichstein, *Helv. Chim. Acta*, **19**, 187 (1936).

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RECEIVED APRIL 24, 1942

## NEW COMPOUNDS

### N,N'-Piperazinium Bis-(2-methyl-5-isopropylbenzenesulfonate)

Smith and Pollard<sup>1</sup> have prepared a number of N,N'-piperazinium bis-(arylsulfonates) and found them moderately soluble in cold water, and quite soluble in hot water. McKee and Bahner<sup>2</sup> found that, while the benzenesulfonate and 2,4-dimethylbenzenesulfonate salts of ethylenediamine and also the 2-methyl-5-isopropylbenzenesulfonate salts of diethylenetriamine and triethylenetetramine are all relatively soluble in water at room temperature, the 2-methyl-5-isopropylbenzenesulfonate salt of ethylenediamine is only slightly soluble. This property was used to separate ethylenediamine from mixtures.

We have prepared N,N'-piperazinium bis-(2-methyl-5-isopropylbenzenesulfonate) and have found that, while it is readily soluble in hot water, it is only slightly more soluble at room temperature than the corresponding salt of ethyl-

enediamine. It is soluble only to the extent of 1 part in 80 of water at 30° or 1 part in 200 at 0°.

The salt was prepared by mixing aqueous solutions of recrystallized sodium 2-methyl-5-isopropylbenzenesulfonate and N,N'-piperazinium dichloride, the former being in excess at all times.<sup>3</sup> The product, obtained in almost the theoretical yield, consisted of small, white leaflets which did not melt below 300°. After recrystallization from water and drying at 110° it was analyzed by the Kjeldahl method.

*Anal.* Calcd. for  $C_{24}H_{48}N_2O_8S_2$ : N, 5.45. Found: N, 5.47, 5.58, 5.64.

(3) We are indebted to Carbide and Carbon Chemicals Corporation for piperazine hexahydrate and to Professor Ralph H. McKee for technical sodium cymenesulfonate used as raw materials for this preparation.

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RECEIVED MARCH 25, 1942

### N-Substituted Piperonylamides

These compounds were prepared by treating a benzene solution of piperonyl chloride with slightly more than two equivalents of the appropriate amine in the same solvent and heating the solution under reflux for thirty minutes. The mixture was treated with water to dissolve the hydrochloride of the amine and the benzene was removed by distillation under reduced pressure with a water pump. The remaining aqueous solution containing the amide in suspension was filtered and the amide washed with water. This procedure was found preferable to distilling separately the benzene solution of the amide as some amides tended to separate from this solvent as an oil. The yield of crude amide was 90% or more in all cases. Purification of the amide was effected by recrystallization from dilute alcohol. The nitrogen determinations were made by the Kjeldahl method.

Name	Formula	M. p., °C. (cor.)	Nitrogen, % Calcd.	Found
N-Phenylpiperonyl- amide	$C_{14}H_{11}NO_2$	146 -147	5.81	5.83
N-( <i>o</i> -Chlorophenyl)- piperonylamide	$C_{14}H_{10}ClNO_2$	107 -108	5.08	5.27
N-( <i>p</i> -Chlorophenyl)- piperonylamide	$C_{14}H_{10}ClNO_2$	206.5-207.5	5.08	5.16
N- <i>o</i> -Tolylpiperonyl- amide	$C_{15}H_{13}NO_2$	137.5-138.5	5.49	5.44
N- <i>m</i> -Tolylpiperonyl- amide	$C_{15}H_{13}NO_2$	121 -122	5.49	5.46
N- <i>p</i> -Tolylpiperonyl- amide	$C_{15}H_{13}NO_2$	149 -149.5	5.49	5.46
N-(1-Naphthyl)- piperonylamide	$C_{18}H_{15}NO_2$	192.5-193	4.81	4.82
N-(2-Naphthyl)- piperonylamide	$C_{18}H_{15}NO_2$	156.5-157.5	4.81	4.60
N-Benzylpiperonyl- amide	$C_{16}H_{15}NO_2$	126.5-127.5	5.49	5.46
N-Cyclohexyl- piperonylamide	$C_{14}H_{17}NO_2$	167.5-168.5	5.67	5.61

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RECEIVED MARCH 9, 1942

(1) Smith and Pollard, *THIS JOURNAL*, **63**, 631 (1941).

(2) McKee and Bahner, U. S. Patent 2,164,587, July 4 1939.