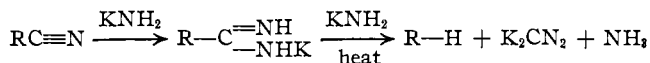


reacting nitrile. It is known that carbon may be converted by the fused amides to cyanamide.¹³

Summary

1. A nickel apparatus has been devised for carrying out reactions in pure fused sodium or potassium amides.

2. The ammono fatty acid anammonides—that is, the nitriles of the fatty acids—react with fused potassium amide in accordance with the type equation



In other words, the salts of the fatty acids of the ammonia system are decomposed by heating with a base of the same system into a hydrocarbon and a sodium ammono carbonate (di-sodium cyanamide). The hydrocarbon R—H is cracked by the molten amide to simpler hydrocarbons and hydrogen, the degree of decomposition increasing with increase in the temperature of the fusion.

3. The failure to obtain the expected hydrocarbon in the reaction $\text{R}-\text{COONa} + \text{NaOH}$ (heated) = $\text{Na}_2\text{CO}_3 + \text{R}-\text{H}$ appears to be due in part at least to the cracking of the expected product R—H to lower hydrocarbons and hydrogen under the catalytic influence of soda lime or sodium hydroxide.

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THE CONSTITUTION OF MELEZITOSE AND TURANOSE

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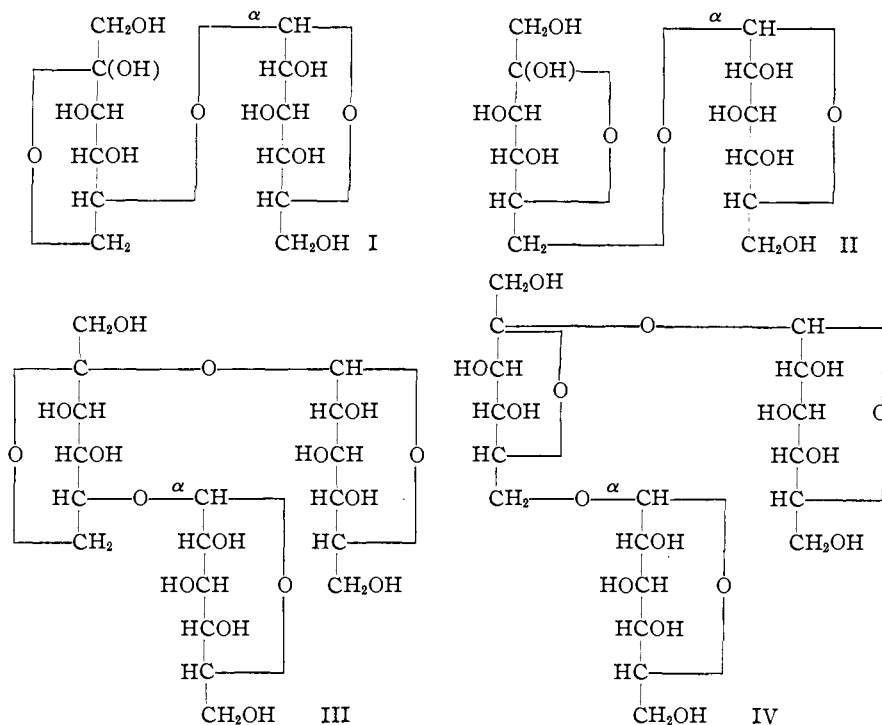
Investigations¹ have shown that when the natural non-reducing trisaccharide melezitose is gently hydrolyzed by weak acid solutions, there results as one of the products the reducing disaccharide, turanose. This sugar is the first known true isomer of sucrose and was first obtained in a pure crystalline condition by C. S. Hudson and the present author.² The failure in the past to secure a crystalline turanose has compelled investigators to use melezitose as the starting material in their efforts to solve the problem of the constitution of these two sugars.

¹³ English Patents 12,219; 21,732 (1894). German Patents 117,623; 124,977; 126,241 (1900); 148,045 (1901). Cf. *Chem. Zentr.*, [I] 75, 411 (1904).

¹ Alekhine, *Ann. phys. chim.*, 18, 532 (1889); G. Tanret, *Bull. soc. chim.*, [3] 35, 816 (1906); R. Kuhn and G. E. von Grundherr, *Ber.*, 59, 1655 (1926).

² C. S. Hudson and E. Pacsu, *Science*, 69, 278 (1929); *THIS JOURNAL*, 52, 2519 (1930).

At the present time two different formulas are assigned for both turanose (I and II) and melezitose (III and IV):



It is my purpose to show that now we can ascribe a definite constitution for these two sugars based on methylation studies of former investigators and on new evidence recently obtained in this Laboratory using crystalline turanose as a starting material.

It is now quite beyond question that the general composition of melezitose is α -glucopyranose <fructose> glucopyranose, where the reducing disaccharide, α -glucopyranose <fructose> is turanose. The α -glycosidic linkage in turanose has been proved by Bridel and Aagaard,³ but the identity of the other potential disaccharide fructose <glucopyranose is not as certain. Unlike turanose it cannot be isolated in a free state. It may be sucrose or a ring isomer of sucrose. Neither will methylation experiments answer this question. A completely methylated melezitose would yield on hydrolysis 2,3,4,6-tetramethylglucopyranose and a trimethylfructose. The structure of this fructose derivative would be the key to the true constitution of melezitose and turanose. Unfortunately, however, none of the theoretically possible isomeric trimethylfructoses has

³ M. Bridel and T. Aagaard, *Bull. soc. chim. biol.*, 9, 884 (1927); T. Aagaard, *Tids. Kemi Bergwesen*, 8, 5, 16, 35 (1928).

so far been prepared, and therefore this direct method of comparison is not available.

If we assume with Zemplén and Braun⁴ that the fructose fragment of melezitose contains the same 2,6-oxide linkage as it was believed exists in the fructose part of sucrose, their conclusion that their partially methylated fructose has the structure of 1,3,4-trimethylfructose <2,6> leads to (I) for the structure of turanose and (III) for melezitose. However, Haworth and Hirst⁵ have shown that the fructose constituent of sucrose does not belong to the normal fructopyranose type and they have suggested the presence of a fructofuranose in sucrose. If such a sucrose be the constituent of melezitose then we must agree, as Zemplén⁶ points out, that the structure of the trimethylfructose is 1,3,4-trimethylfructose <2,5> and therefore turanose and melezitose should be represented by (II) and (IV), respectively. The trimethylfructose in question has been methylated by Leitch⁷ and 1,3,4,6-tetramethylfructose <2,5> was obtained. This same fructose derivative is claimed by Haworth to be found when octamethylsucrose is hydrolyzed. According to Leitch this result is evidence that Zemplén's assumption that sucrose is the non-reducing potential disaccharide of melezitose is correct and that therefore the structure of turanose and melezitose must be (II) and (III). However, reflection will show that this conclusion is not justified. If we consider the possibility that 1,3,4-trimethylfructose may easily acquire two different rings,⁸ it is possible that the non-reducing disaccharide in melezitose is not the common sucrose but rather a ring isomer containing a 2,6-oxygen bridge in the fructose component. The completely methylated derivative of such a melezitose (III) still may yield on hydrolysis 1,3,4-trimethylfructose <2,5> because the expected 1,3,4-trimethylfructose <2,6> may easily shift its pyranoid ring into a furanoid ring.

Further evidence which leads us to doubt that ordinary sucrose is a constituent of the melezitose molecule is found in certain investigations of Bridel and Aagaard⁹ on the hydrolysis of melezitose by various enzymes.

It therefore appears that the "proved" structures of melezitose and turanose are still questionable. Indeed experiments which I am now reporting indicate that the structures originally assigned to these sugars by Zemplén and Braun are the more probable.

It has been shown by Helferich⁹ in his studies on triphenylmethyl deriva-

⁴ G. Zemplén and G. Braun, *Ber.*, **59**, 2230 (1926).

⁵ W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, 1858 (1926).

⁶ G. Zemplén, *Ber.*, **59**, 2539 (1926).

⁷ Grace Leitch, *J. Chem. Soc.*, 588 (1927).

⁸ This is a logical assumption since the potential ketone group as well as the fifth and sixth OH groups are free.

⁹ B. Helferich and J. Becker, *Ann.*, **440**, 1 (1924); B. Helferich, L. Moog and A. Jünger, *Ber.*, **58**, 872 (1925).

tives of the sugars and glucosides that triphenylchloromethane reacts only with the primary alcoholic groups in these compounds. It is evident, therefore, that triphenylchloromethane may be used to advantage in investigating the structure of turanose. The quantity of this reagent taken up by the sugar will give us an indication of the number of primary alcoholic groups present in the molecule. This method has been used by Josephson¹⁰ in his studies on maltose, sucrose and raffinose. He has shown that hydrogen bromide dissolved in glacial acetic acid easily removes the triphenylmethyl residue as triphenylbromomethane and, if this be determined quantitatively, the number of primary alcoholic groups can be readily ascertained.

If we apply this method of analysis to turanose, certain possibilities suggest themselves. If formula (II) be correct, a di-(triphenylmethyl)-turanose will be obtained. However, if the correct structure of turanose be that represented by formula (I), a tri-(triphenylmethyl)-turanose may result inasmuch as the sixth OH group of the fructose residue though involved in ring formation may become free due to a shift of the ring. That such a ring shift may be expected is justified by the observation of Josephson.¹⁰ This investigator has shown that both arabinose and xylose in their normal forms react slowly with triphenylchloromethane in pyridine solution.

Experiments carried out with crystalline turanose show that this sugar readily combines with triphenylchloromethane to give a tri-(triphenylmethyl)-turanose which on acetylation yields a pentaacetyl derivative. These facts point clearly to the conclusion that the glucose residue in the turanose molecule cannot be attached to the sixth carbon atom of the fructose constituent. This obviously rules out formula (II) for the constitution of the turanose component in melezitose and also indicates that the true constitution of melezitose is as represented by formula (III). Such a formula for melezitose confirms the above statement that the potential non-reducing disaccharide in the molecule is not sucrose but rather a ring isomer of it. As regards the structure of the free turanose we can state with some degree of certainty that it is a 5- α -glucosido<1,5>fructose containing a 2,4-ring in its fructose part or a 2,6-ring which in solution shifts into the 2,4-position. That such a ring shift takes place is supported by evidence which will be published later. If turanose be acetylated in acetic anhydride solution at room temperature in the presence of the catalyst zinc chloride, three well-defined crystalline octaacetates are produced instead of the two foreseen by theory if a ring shift is excluded.

Finally it may be added that the fact that all the known disaccharides are linked either to the fourth or sixth carbon atom and never to the fifth position should not concern us seriously if it be observed that the fifth

¹⁰ K. Josephson, *Ann.*, **472**, 230 (1929).

carbon atom of fructose where the glycosidic linkage in the turanose molecule occurs is in reality the fourth carbon atom counted from the potential reducing group of the fructose component.

Experimental Part

Preparation of Tri-(triphenylmethyl)-turanose.—Three and a half grams of crystalline turanose was dissolved in 60 cc. of hot pyridine and to the cooled solution 14 g. of triphenylchloromethane was added. On standing for a short time at room temperature a white crystalline material was deposited from the solution which in all probability is triphenylmethyl pyridine chloride. After four to five days the solution was cooled in an ice-bath and water was added to it drop by drop. When the double compound went into solution, more water was carefully added until cloudiness developed. The liquid was kept below 0° for several hours and the triphenylcarbinol which separated during this time removed by filtration. The clear filtrate was poured under vigorous stirring into one and one-half liters of ice water. The gummy precipitate so obtained was allowed to stand for several days in water which was occasionally renewed. At the end of this time the gummy precipitate had changed into a white, solid mass. This was collected at the pump, dissolved in alcohol, the solution decolorized with charcoal and stirred into a large amount of ice water. After standing for two days in the ice box the treatment was repeated. Finally it was filtered and dried for several days at room temperature over phosphorus pentoxide in a vacuum desiccator to constant weight; yield, 2-3 g. of colorless, white powder. The specific rotation was found to be $[\alpha]_D^{20}$ 30.87° (0.7046 g. in 25 cc. of chloroform solution rotated 1.74° to the right in a 2-dm. tube). No mutarotation of the solution could be observed. This material melted at 105-115°, a phenomenon which is due to the presence of the α - and β -forms. It is insoluble in water and petroleum ether but is readily soluble in the common organic solvents.

Anal. Calcd. for di-(triphenylmethyl)-turanose, $C_{50}H_{50}O_{11}$: C, 72.60, H, 6.10; for tri-(triphenylmethyl)-turanose, $C_{69}H_{64}O_{11}$: C, 77.50, H, 6.04. Found: C, 77.06; H, 6.21.

Preparation of Tri-(triphenylmethyl)-turanose Pentaacetate.—Two grams of tri-(triphenylmethyl)-turanose was dissolved in 10 cc. of pyridine and to the ice-cold solution 6 cc. of acetic anhydride was added. On standing for two days at room temperature a few drops of water were carefully added to the cooled solution and after half an hour it was stirred into 500 cc. of ice water. The sirup which was precipitated very soon turned into a solid. This was allowed to stand for several days in water which was occasionally changed. The filtered substance was then dissolved in alcohol, the solution decolorized with charcoal and stirred into ice water. After repeating this treatment the filtered substance was dried in a vacuum desiccator over phosphorus pentoxide and solid sodium hydroxide to constant weight: yield, 2.2 g. of colorless fine powder having a specific rotation in chloroform of $[\alpha]_D^{20}$ 75.85° (0.6889 g. in 25 cc. of chloroform solution rotated 4.18° to the right in a 2-dm. tube). The substance does not possess a sharp melting point as it begins to sinter at about 85° and melts at 95-105°. It is insoluble in water but is soluble in the common organic solvents except petroleum ether.

Anal. Calcd. for di-(triphenylmethyl)-turanose hexaacetate, $C_{62}H_{62}O_{17}$: C, 68.98; H, 5.79; for tri-(triphenylmethyl)-turanose pentaacetate, $C_{79}H_{74}O_{16}$: C, 74.14; H, 5.83. Found: C, 73.92; H, 5.93.

In an acetyl estimation made by the method of Kunz,¹¹ 0.4060 g. of substance was dissolved in 80 cc. of pure acetone to which 24.6 cc. of 0.1 *N* sodium hydroxide was sub-

¹¹ A. Kunz and C. S. Hudson, *THIS JOURNAL*, **48**, 1982 (1926).

sequently added. The acetylated triphenylmethyl derivative of turanose neutralized 16.8 cc. of decinormal alkali, whereas the value calculated for tri-(triphenylmethyl)-turanose pentaacetate is 15.9.

The triphenylmethyl estimation was carried out by the method of Josephson,¹⁰ 0.1525 g. of substance was dissolved in 0.5 cc. of cold glacial acetic acid and mixed with 0.4 cc. of glacial acetic acid saturated at 0° with hydrogen bromide. After a transitory halochromic coloration due to the formation of a double compound between triphenyl carbinol and hydrogen bromide, triphenylbromomethane separated from the cold liquid. The crystals were collected on a Jena glass filter and washed by means of a pipet with 0.4 cc. of glacial acetic acid. After being dried over solid potassium hydroxide in a vacuum desiccator to constant weight, the triphenylbromomethane formed weighed 0.1088 g., which is 94.13% of the theoretical amount required for tri-(triphenylmethyl)-turanose pentaacetate.

Summary

Two different formulas for both turanose and melezitose are recorded in the literature. Evidence is submitted to show that turanose has three primary alcoholic groups in its molecule in that a tri-(triphenylmethyl)-turanose and its pentaacetate could be prepared. This fact together with certain methylation experiments of former investigators leads to the conclusion that the formulas of turanose (I) and melezitose (III) originally suggested by G. Zemplén and G. Braun should be chosen for these rare conipound sugars.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MUNICH
AND THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYL COMPOUNDS. THE RESOLUTION OF 8,8'-DICARBOXY-1,1'-DINAPHTHYL

By W. M. STANLEY¹

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The resolution of 2,2'-dicarboxy-1,1'-dinaphthyl² (I) demonstrated that the 2,2'-carboxyl groups and the 8,8'-hydrogen atoms are sufficiently large to interfere with each other and thus allow resolution into optical isomers. This indicates that a carboxyl group and a hydrogen atom are large enough to interfere across the space AB (III) which may be calculated as 2.51 Å. by assuming the usual angles in the benzene ring. The fact that this compound was found to be quite stable toward racemization indicates that this interference is fairly large. The compound in which the carboxyl groups and the hydrogen atoms are interchanged, 8,8'-dicarboxy-1,1'-dinaphthyl (II), should also be resolvable, since the 8,8'-carboxyl groups and the 2,2'-hydrogen atoms should interfere across the space AB as in the previous compound, assuming that no additional fac-

¹ National Research Fellow in Chemistry.

² Kuhn and Albrecht, *Ann.*, **464**, 282 (1928).