192.6° to 192.7° at 738.4 mm.,[10] 195° at 767 mm.,[11] 194.0°[7] and 193.1°;[8] for monoethylaniline, 206.0° at 760 mm.,[6] 205.0°[7] and 204.0°;[8] and for diethylaniline, 216° to 217° at 769.5 mm.,[11] 216.0°[7] and 215.5°.[8]

Kahlbaum[8] appears to be the only one who has determined the vapor pressures of these compounds. The methods he used and the results he obtained on these and other compounds have been fully discussed by Smith and Menzies[1] and by Schmidt.[12] These discussions or criticisms direct attention to several facts about his method, which show it to be at fault for the accurate determination of vapor pressures.

Summary

The vapor pressures and boiling points of mono- and dimethylanilines and mono- and diethylanilines have been redetermined by the method devised by Smith and Menzies. The boiling points found for the mono- and dimethyl- and mono- and diethylanilines were 195.70°, 193.50°, 204.72° and 216.27°, respectively, at 760 mm.

[Contribution from the Polarimetry Section of the Bureau of Standards, United States Department of Commerce[1]]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. IX.[2] THE ROTATION OF THE ALPHA FORM OF METHYL GENTIOBIOSIDE RECENTLY SYNTHESIZED BY HELFERICH AND BECKER

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In 1917 Hudson and Johnson[3] showed that the rotations of several derivatives of gentiobiose could be calculated, including the alpha and beta forms of methyl gentiobioside, the hepta-acetates of these glycosides, and the alpha form of gentiobiose octa-acetate. They prepared for the first time three of these five substances and found a good agreement between the calculated and observed rotations, as follows: α-gentiobiose octa-acetate, obs. +52° (in chloroform), calcd. +52°; β-methyl gentiobioside, obs. —36° (in water), calcd. —38°; β-methyl gentiobioside hepta-acetate, obs. —19° (in chloroform), calcd. —17°. The alpha form of methyl gentiobioside and its hepta-acetate were unknown and were not prepared because of the lack of a suitable method of synthesis for this alpha glycoside,

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[10] Brühl, *Ann.*, **235**, 14 (1886).

[11] Schiff, *Z. physik. Chem.*, **1**, 383 (1887).

[12] Schmidt, *ibid.*, **8**, 629 (1891).

[1] Published by permission of the Director of the Bureau of Standards.

[2] Part VIII was published in This Journal, **47**, 537 (1925).

[3] *Ibid.*, 39, 1271 (1917).

but the rotations of these substances were calculated to be, for α-methyl gentiobioside, +65 in water, and for its hepta-acetate, +66 in chloroform.

Helferich and Becker[4] have recently synthesized a substance which they regard as alpha methyl gentiobioside. It crystallizes with one molecule of alcohol of crystallization, and they record two measurements of its rotatory power, one referring to the substance after drying over phosphorus pentoxide at the relatively high temperature of 142° ($[\alpha]_D^{23} = +61.8$ in water) and the other referring to the substance containing alcohol of crystallization (11.4% of alcohol) ($[\alpha]_D^{24} = +59.4$ in water). If the latter measurement be referred to dry material $[\alpha]_D^{24} = +67.0$. They mention (p. 7) that the limit of error in these determinations is considerable because a sensitive polariscope was not available for their use. The average of their results, $[\alpha]_D = +64$ for α-methyl gentiobioside in aqueous solution, agrees satisfactorily with the rotation that Hudson and Johnson calculated (+65). Doubtless it will be only a matter of time before the rotation of α-methyl gentiobioside hepta-acetate in chloroform solution can likewise be measured.

The alpha and beta forms of methyl gentiobioside constitute the first known pair of methyl glycosides of a disaccharide, and the agreement of their observed rotations with those calculated from the rotations of the alpha and beta forms of methyl glucoside on the assumption of van't Hoff's principle of optical superposition is a good indication that the method of comparing structures with rotatory powers that is based upon this principle can be extensively employed in structural studies of the sugars and their derivatives. In the present instance, this method furnishes valuable and independent evidence that the substance which Helferich and Becker have synthesized is what they suppose it to be, namely, α-methyl gentiobioside. This evidence is very welcome in the present instance because it confirms in an independent way the chemical evidence (synthetic method, action of enzymes, etc.) by which Helferich and Becker have determined the constitution of the compound.

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[4] Helferich and Becker, *Ann.*, **440**, 1 (1924).