have been studied chemically heretofore. Wax-like products were obtained in variable but small quantities from all of the 21 species. In none of these was the percentage found in excess of ten and some of it may have been derived from the epidermal cells rather than the secreting hairs.

Summary

Flavone was found to form at least 75% of the farina of twenty-one species of primula, by heating with 6 *N* hydrochloric acid, filtering the hot solution, cooling to 20° and separating the $C_{15}H_{10}O_2 \cdot HCl \cdot H_2O$ formed. The farina of *P. denticulata* contained about 10% of an orange-yellow compound, $C_{15}H_{10}O_4$, which melted at 228° and behaved like an undescribed dihydroxyflavone. A second yellow compound, $C_{15}H_{10}O_3$, which melted at 153° was separated from *P. verticillata*. Varying amounts of wax-like components were found in all the twenty-one species.

BERKELEY, CALIF. RECEIVED OCTOBER 25, 1944

NOTES

Bis-(trimethylenediamino)-cupric Sulfate

BY LAWRENCE H. AMUNDSEN[1] AND LENA A. MALENTACCHI

This substance was prepared for use as a germicide in the treatment of surface tissues by iontophoresis after the desired combination of properties had not been found in a number of other copper compounds, including the corresponding one from ethylenediamine. A report on these tests is expected to appear soon.[2]

Bis-(trimethylenediamino)-cupric sulfate is obtained readily from trimethylenediamine and cupric sulfate, either anhydrous (blue) or as a monohydrate (pinkish-purple). The hydrate is the stable form under ordinary conditions but loses water slowly at 56° and promptly at 100°. At room temperature it dehydrates in a desiccator over calcium sulfate (Drierite). The hydrate absorbs no more water under the atmospheric conditions prevailing in the laboratory except in the most humid summer weather, when some samples gained as much as 4–5% in weight. It is very soluble in water.

Experimental

Trimethylenediamine.—A solution was prepared from 882.4 g. (7.81 moles) of trimethylene chloride, 12636 cc. (187.4 moles) of ammonium hydroxide, and 7 liters of 95% ethanol and left standing in a stoppered bottle at room temperature (19–22°), samples being withdrawn at weekly intervals for determinations of ionizable chlorine (Table I). After five weeks the mixture was distilled to dryness under the vacuum of a water-jet pump (13 mm.). After the addition of 1637 cc. (31.24 moles) of 50% sodium hydroxide the mixture again was distilled to dryness under vacuum. The distillate was collected in two fractions of 873 cc. and 720 cc., respectively. Water (220 cc.) was added to the residue and a third fraction was obtained by distilling to dryness again. The three fractions were saturated with sodium hydroxide. The upper layer was separated from each and dried over sodium hydroxide. The layers were separated again and more sodium hydroxide was added to the upper layers. This process was repeated until fresh sodium hydroxide remained unchanged when added to the products. Upon rectification through a 180-cm. column packed with glass helices, 161 g. of trimethylenediamine was obtained from the first fraction and 21.5 g. from the second, making a yield of 32% of the theoretical. No attempt was made to rectify the product from the third fraction because of its high viscosity and because of the low yield from even the second fraction. It presumably consisted largely of amines of higher molecular weight. The trimethylenediamine was collected at 48–50° at 20 mm. It boiled at 133° cor. at 754.5 mm.[3,4] The pressure was reduced to 5 mm. and the distillation was continued as long as any liquid would come over. When 21 cc. of material so obtained was rectified again in a semimicro apparatus,[5] 9.4 g. of a product boiling at 128–131.5° at 20 mm. was obtained (b. p. 230.5° cor. at 760.2 mm.[2]). This compound is presumed to be bis-(γ-aminopropyl)-amine, which von Braun[4] reported that he obtained as a fraction boiling from 210–230°.

TABLE I

YIELD OF CHLORIDE ION

Reaction period, days	% Theor.
7	33
14	63
21	82
28	88
35	92

Bis-(trimethylenediamino)-cupric Sulfate.—A mixture of 15.4 g. (0.208 mole) of trimethylenediamine, 24.97 g. (0.1 mole) of C. P. cupric sulfate pentahydrate, and 15 cc. of water was boiled gently under a reflux condenser until all of the copper sulfate went into solution. The mixture then was placed in a vacuum desiccator over calcium chloride. From time to time the crust on the surface was broken up, and the drying was continued until there was no further loss in weight. The product was the monohydrate (Table II).

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[2] By Commander Armand J. Pereyra, Medical Corps, U. S. Navy.

[3] The determination was made by the micro method described in Shriner and Fuson's, "Identification of Organic Compounds," second edition, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 93.

[4] Fisher and Koch (*Ber.*, **17**, 1799 (1884)) reported 135–136° at 738 mm.; Putokhin (*Trans. Inst. Pure Chem. Reagents* (Moscow) No. 6, 10 (1927)), 135–136°; von Braun, *et al.* (*Ber.*, **70B**, 979 (1937)), 136–138°; Aspinall (THIS JOURNAL, **63**, 2843 (1941)), 131° at 760 mm.; Whitmore, *et al.* (*ibid.*, **66**, 725 (1944)), 138° at 735 mm. The higher boiling points may have been determined on samples that were not completely dry. Tests made during the present study showed that the boiling point was raised by the addition of a little water and, furthermore, that the apparent boiling point would be several degrees higher than reported above if the sample was exposed to the atmosphere of the laboratory for a few minutes during the determination.

[5] Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

TABLE II

ANALYSIS OF BIS-(TRIMETHYLENEDIAMINO)-CUPRIC SULFATE HYDRATE[6]

	% C	% H	% Cu	% N	% S
Calcd. for $C_6H_{20}CuN_4SO_4·H_2O$	22.11	6.81	19.51	17.19	9.84
Determined	21.88	6.40	19.51	16.80	9.66
Determined	21.98	6.44	19.69	16.54	9.99

When heated it changes to the blue anhydrous form and finally decomposes at 276–277° cor. with evolution of gas, leaving a brown residue. Samples of the hydrate were heated to 35, 57, 78 and 100° and kept at these temperatures, all samples being reweighed after 1, 3, 8, 10, and 14 days. At 35° there was no dehydration. At 57° dehydration progressed so slowly that it was not quite complete even after fourteen days. At both 78 and 100° the dehydration was complete after one day. At 100° the change appeared to take place instantly, but at 78° even the visible color change required about an hour. The anhydrous compound apparently is stable at 100° for no additional change in weight occurred during the fourteen-day period of heating. The product does not contain unreacted cupric sulfate because when a sample of it was treated with additional trimethylenediamine and water and dried, it went back to its original weight.

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(6) All determinations were made by the Laboratory of Microchemistry, 366 Fifth Avenue, New York, N. Y.

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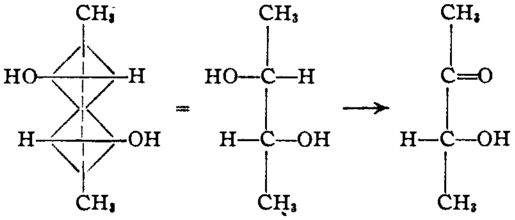
Configuration of Acetylmethylcarbinol

BY R. H. BLOM

The configurations of the optically active 2,3-butylene glycols have recently been correlated with the configurational system which Emil Fischer established for glucose, as D-(−) and L-(+)- for the levo- and dextro-rotatory forms, respectively.[1] The proof depends upon the established relationship of configuration between the methylethylcarbinols and the lactic acids.[2] In turn, the place of the lactic acids in the Fischer sugar system follows, for example, from the oxidation of the methyl 6-desoxy-hexopyranosides to the corresponding lactic acids.[3] In studying the vapor-phase oxidation of D-(−)-2,3-butylene glycol (I), it has been found that the acetylmethylcarbinol so formed (II) is levorotatory. Although extensive racemization occurred during the reaction, the rotation of the product was sufficient to establish the configurational relationship. Since the glycol and the carbinol can exist in only two active forms, D- or L-, racemization would form only the racemic structures in both cases. The acetylmethylcarbinols and the 2,3-butylene glycols which exhibit the same sign of rotation therefore possess the same configuration:



I II

D-(−)-2,3-Butylene glycol[4] D-(−)-Acetylmethylcarbinol

A sample of D-(−)-2,3-butylene glycol,[5] $[\alpha]^{21}\text{D}$ −12.20° (C = 100%, 1-dcm. tube) was heated to 140° and vaporized by means of a stream of air. The vapors were passed through a Pyrex tube packed with copper turnings and maintained at 315°. On condensation and fractional distillation, the main products obtained were diacetyl (33% yield), b. r. 88–88.5° (uncor.) and acetylmethylcarbinol (25% yield), b. r. 142–144° (uncor.), $n^{21}\text{D}$ 1.4186, which values are in good agreement with the literature.[6] The latter was levorotatory, $[\alpha]^{21}\text{D}$ −1.39° (C = 100%, 1-dcm. tube). On standing for twenty-four hours at 4° crystals of the optically inactive dimer of acetylmethylcarbinol were deposited.[7] Since an optically pure isomer of acetylmethylcarbinol has not yet been conclusively obtained,[8] it is not possible to calculate the concentration of the active form present in the product. The acetylmethylcarbinol was identified by acetylation with acetic anhydride, acetoin acetate, b. r. 167–168°[9] being obtained.

The assistance of Dr. S. A. Morell in the preparation of this paper is gratefully acknowledged.

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(1) S. A. Morell and A. H. Auernheimer, THIS JOURNAL, **66**, 792 (1944).

(2) P. A. Levene, A. Walti and H. L. Haller, *J. Biol. Chem.*, **71**, 465 (1927).

(3) W. D. Maclay, R. M. Hann and C. S. Hudson, THIS JOURNAL, **61**, 1660 (1939).

(4) The structural formulas used conform with the fundamental convention of Emil Fischer in that the lower edges of the tetrahedra lie in a straight line in the plane of the paper, the corners which carry (H) and (OH) groups thus being above the paper.

(5) G. E. Ward, O. G. Pettijohn, L. B. Lockwood and R. D. Coghill, THIS JOURNAL, **66**, 541 (1944).

(6) J. R. Pound and A. M. Wilson, *J. Phys. Chem.*, **39**, 1135 (1935).

(7) T. M. Lowry and W. C. G. Baldwin, *J. Chem. Soc.*, 704 (1935).

(8) W. Dirscherl and A. Schollig, *Ber.*, **71**, 418 (1938).

(9) M. Bergmann and S. Ludewig, *Ann.*, **436**, 173 (1924).

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Carbobenzoxy Derivatives of Aromatic Amines

BY NORMAN C. BERGSTROM AND A. E. MARTELL[1]

A number of aromatic amines were treated with benzyl chlorocarbonate in order to determine the ease of acylation and the possible use of the reagent for obtaining crystalline derivatives of amines. The acylation of amines and amino acids with benzyl chlorocarbonate has been thoroughly described by Bergmann[2] and his method is essentially the one used here.

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(1) Now at Clark University, Worcester, Mass.

(2) Bergmann and Zervas, *Ber.*, **65**, 1192 (1932).