[CONTRIBUTION FROM THE HICKRILL CHEMICAL RESEARCH FOUNDATION AND THE DEPARTMENT OF CHEMISTRY, BROOKHAVEN NATIONAL LABORATORY]

The Structural Fate of the Carbonyl Carbon Atom in the Tropolone–Benzoic Acid Rearrangement[1]

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The rearrangement of 2,4,7-tribromotropone and 2,7-dibromotropone, both labeled in the carbonyl group with C^{14}, has given 2,4- (and 2,5-)-dibromobenzoic acid and 2-bromobenzoic acid, respectively, with all the radioactivity in the carboxyl group. It is concluded that the carbon atom of the carboxyl group is derived from the carbonyl group in rearrangements of tropolone (and derivatives) to benzoic acid (and derivatives). In the ring enlargement of ketones by diazomethane it has been shown incidentally that the carbonyl group retains its integrity during rearrangement.

The structural characteristic of the rearrangement of tropolone and derivatives to benzoic acid and derivatives has been abundantly documented,[3] the single reported inconsistency[4,5] having been invalidated.[6] The carbonyl carbon atom and the adjacent carbon atom, bearing the Lewis base lost in the rearrangement, become the carboxyl carbon and C_1 of the benzoic acid. It is not known, however, whether the carboxyl carbon of the benzoic acid is derived from the carbonyl carbon or the adjacent C_2 of the tropolone ring. The present work purposes to resolve this structure ambiguity by using radioactive carbon to distinguish between the relevant atoms.

The structure of the starting material in the two series of experiments was established unequivocally as cyclohexanone-1-C^{14} by its conversion on two successive treatments with hydrazoic acid to the dibenzamide of pentamethylene diamine with an activity indistinguishable from background.

Cyclohexanone-1-C^{14} was then converted by the reaction with diazomethane to cycloheptanone-1-C^{14} from which 2,4,7-tribromotropone-1-C^{14} was prepared[7,8] by the two-step procedure of Doering and Sayigh.[6] The reduction of tribromotropone-1-C^{14} to tropone-1-C^{14} was effected catalytically according to Dauben and Ringold.[7,9] The bromination of tropone-1-C^{14} reported by Nozoe, *et al.*,[10] was effected by a procedure of Doering and Detert[11] to give 2,7-dibromotropone-1-C^{14} which was then rearranged with alcoholic alkali to *o*-bromobenzoic acid-carboxyl-C^{14}. Treatment of this acid with hydrazoic acid afforded barium carbonate containing all of the radioactivity and benz-*o*-bromoanilide with an activity at background.

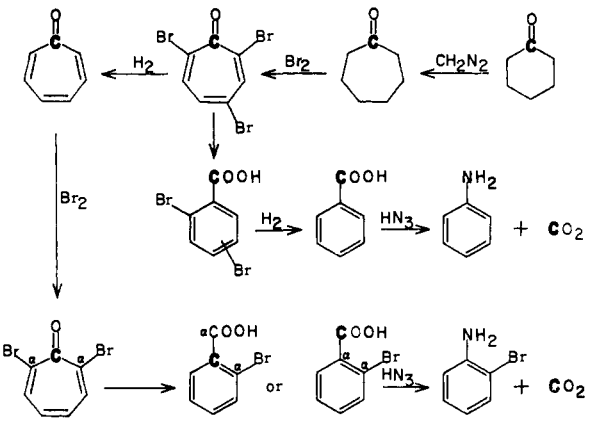

Fig. 1.

Two conclusions can be drawn from this clear-cut outcome neither of which could have been drawn without further experimental evidence if radioactivity had appeared in both the carbon dioxide and the benzbromoanilide. The assignment of the structural distribution of C^{14} in the compounds intermediate between cyclohexanone-1-C^{14} and *o*-bromobenzoic acid-carboxyl-C^{14} depends critically on the assumption that the reaction of cyclohexanone-1-C^{14} gives cycloheptanone-1-C^{14}. Had this assumption been false and some or all of the C^{14} been located elsewhere in the cycloheptanone molecule, the carboxylic acid group of the *o*-bromobenzoic acid could not have contained all of the C^{14}. Such C^{14} as resided elsewhere in the 2,7-dibromotropone (and cycloheptanone) would have been symmetrically distributed with the consequence that half of the radioactivity would have remained in the benz-*o*-bromanilide, even in the hypothetical situation where the radioactivity was distributed between the 2- and 7-positions and the mechanism of the aromatization had involved C_2 becoming the carbon atom of the carboxylic acid group.

Location of C^{14} in the cycloheptanone being entirely at the 1-position, it is clear that the carbonyl group of cyclohexanone remained the carbonyl group in the cycloheptanone formed on ring enlargement with diazomethane. This result, certainty not unexpected, is in complete harmony with the results of a similar study of the Wolff rearrangement.[12]

Secondly, it can be concluded that the C_1 carbon

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

(2) Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

(3) Examples of rearrangement in which the structure of the substituted tropolone is known independently of rearrangement include purpurogallin, 3,4-benztropolone, stipitatic acid, γ-thujaplicin and 4-methyltropolone. These are all referred to by J. W. Cook and J. D. Loudon, *Quart. Revs. (London)*, **5**, 99 (1951).

(4) T. Nozoe, Y. Kitahara, S. Masamune and S. Yamaguchi, *Proc. Japan Acad.*, **28**, 85 (1952).

(5) T. Nozoe, S. Seto and T. Sato, *ibid.*, **30**, 473 (1954).

(6) W. von E. Doering and A. A. R. Sayigh, THIS JOURNAL, **76**, 39 (1954).

(7) H. J. Dauben and H. J. Ringold, *ibid.*, **73**, 876 (1951).

(8) T. Nozoe, Y. Kitahara, T. Ando and S. Masamune, *Proc. Japan Acad.*, **27**, 415 (1951).

(9) Dr. H. J. Ringold very generously furnished us with the experimental details of the reduction procedure.

(10) T. Nozoe, T. Mukai, K. Takase and T. Nagase, THIS JOURNAL, **28**, 477 (1952).

(11) W. von E. Doering and F. L. Detert, unpublished work.

(12) C. Huggett, R. T. Arnold and T. I. Taylor, THIS JOURNAL, **64**, 3043 (1942).

atom of the carbonyl group of 2,7-dibromotropone becomes the carbon atom of the carboxylic acid group in the rearrangement product, *o*-bromobenzoic acid.

The second example involves rearrangement of 2,4,7-tribromotropone-1-C^{14} with alkali to a mixture of 2,4- and 2,5-dibromobenzoic acids. These were reduced to benzoic acid from which radioactive barium carbonate and inactive benzanilide were obtained by the Schmidt reaction. Here, likewise, the carbonyl carbon of the tropone becomes the carboxyl carbon in the rearranged acid.

The imposition of this new structural condition excludes all mechanistic hypotheses in which a carbon atom other than the carbonyl carbon emerges from the ring to become the carboxyl group. We see no reason to doubt that the same condition applies where other reagents such as ammonia and alkoxide ion effect the rearrangement and where other groups such as methoxyl, alkoxyl and the halides are the displaced substituent. In particular the second hypothesis proposed by Doering and Knox[13] can no longer be considered whereas all the other mechanisms[14] proposed are consistent with the new structural condition.

As indicated earlier by Doering and Knox[13] these mechanisms are inconsistent with the implications inherent in the rearrangement of molecules such as 3,5,7-tribromotropolone methyl ether[13] and 3,7-dibromotropolone methyl ether.[17] These rearrangements take two paths, the one as the rearrangement of a tropolone methyl ether with elimination of methoxide ion and the formation of 2,4,6-tribromo-(and 2,6-dibromo)-benzoic acids, the other as the rearrangement of a bromotropone with the elimination of bromide ion and the formation of 2-methoxy-3,5-dibromo-(and 3-bromo)-benzoic acids. It seemed most surprising to us (although not to Johnson[19] or Nozoe[17] and Seto[20]) that the elimination of the relatively strong base, methoxide ion, was actually favored over the elimination of the relatively weak base, bromide ion.

In a general way, this inconsistency can be removed by mechanistic hypotheses in which breaking of the carbon–methoxyl or carbon–bromine bonds—that is, the elimination step—is not a part of the product-determining transition state. The earlier specific scheme embodying this general principle has now been shown to be incompatible with the isotope experiment and therefore untenable.[13]

The Faworski modification of the C_1, single-transition-state mechanism,[14b] itself incompatible with the condition of "insensitivity to base-strength of leaving substituent," can be made consistent by assigning a separate transition state to the elimination step. This procedure introduces a new intermediate (A and B) as a barrier to prevent the preceding, product-determining transition state (a and b) sensing the relative advantage of losing X^- or Y^-. The new intermediate is quite similar to that proposed for ordinary nucleophilic displacements on aromatic compounds.[22] In these terms the product composition is determined by the relative free energies of the transition states a and b leading to the intermediates A and B.

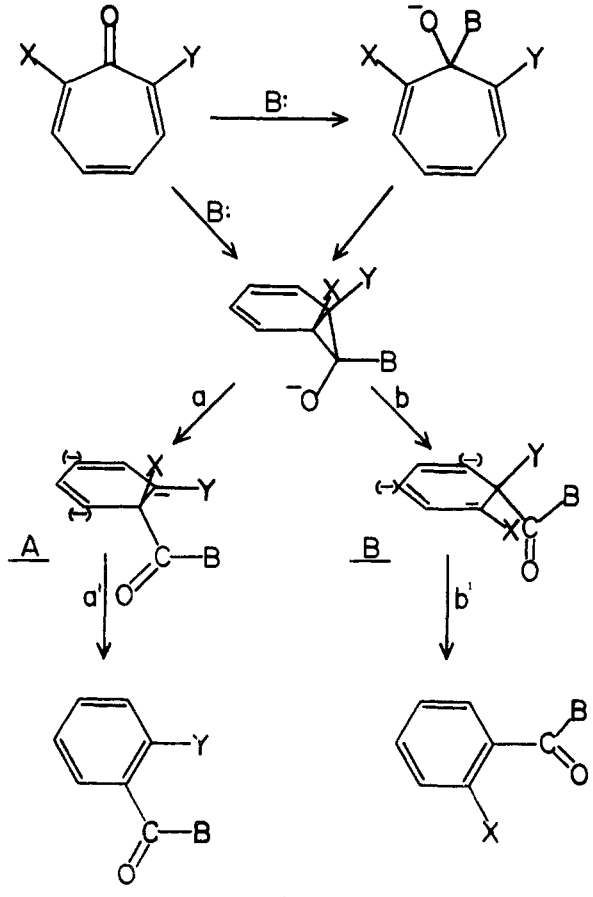

Fig. 2.

In the rearrangement of the tribromotropolone methyl ether, for example, a small resonance factor favors the formation of tribromobenzoic acid whereas a small steric factor favors the formation of methoxydibromobenzoic acid. In this and related examples,[6,23,24] the energy factors are apparently small and opposed in effect. In 3-nitrotropolones, the resonance factor should be overriding. Consistently there are no examples of

(13) W. von E. Doering and L. H. Knox, THIS JOURNAL, **74**, 5683 (1952).

(14) (a) "C_1-single transition state mechanism": attack of the base at C_1 followed by a suitable shift of electrons, bond angles and distances with the simultaneous ejection of the leaving base.[15-20] (b) "C_1 Faworski-type, single-transition-state mechanism": similar to 14(a), it hypothesizes attack at C_1, valence-bond tautomerization to a cyclopropane-containing, norcaradiene derivative followed by a Faworski rearrangement[21] involving a single transition state.[18] (c) "C_2 single-transition-state mechanism": attack at C_2 followed by rearrangement to an acylium cation in which C_1 has become exocyclic to the ring.[18]

(15) W. von E. Doering and L. H. Knox, THIS JOURNAL, **73**, 828 (1951).

(16) R. D. Haworth and P. R. Jeffries, *J. Chem. Soc.*, 2067 (1951).

(17) T. Nozoe, Y. Kitahara and S. Masamune, *Proc. Japan Acad.*, **27**, 649 (1951).

(18) P. Akroyd, R. D. Haworth and P. R. Jeffries, *J. Chem. Soc.*, 286 (1954).

(19) A. W. Johnson, *ibid.*, 1131 (1954).

(20) S. Seto, *Science Rep. Tohoku Univ. First Ser.*, **37**, 377 (1953).

(21) R. B. Loftfield, THIS JOURNAL, **72**, 632 (1950).

(22) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(23) T. Nozoe, S. Seto, H. Takeda, S. Morosawa and K. Matsumoto, *Proc. Japan Acad.*, **28**, 192 (1952).

(24) T. Nozoe, S. Seto and S. Matsumura, *ibid.*, **28**, 410 (1952).

the loss of nitrite ion in the rearrangements of such molecules.[25,26] Unfortunately, nowhere in the literature is there a pair of molecules such as 2-methoxy-4-nitro-7-bromotropone and 2-methoxy-5-nitro-7-bromotropone, the behavior of which on rearrangement would test more critically the modified, Faworski-type, double-transition-state mechanism.

We wish to express our deep appreciation of the generous and indispensable assistance given us by Drs. R. Christian Anderson and D. R. Christman and Miss Nancy E. Day, Chemistry Department of the Brookhaven National Laboratory.

Experimental

The analytical and counting procedure for C^{14} were those devised by Anderson, Delabarre and Bothner-By.[27] The standard deviation for a given assay is 1–2% while the sum of all the errors inherent in the analysis is not greater than 5%.

Cyclohexanone-1-C^{14}.—Radioactive cyclohexanone-1-C^{14} (5 ml.)[28] was diluted with 120 ml. of inactive cyclohexanone to give a sample (1.42 mμc./mg. C) which was fractionally distilled to give cyclohexanone-1-C^{14}, b.p. 149–150° (1.30 mμc./mg. C; 7.80 mμc./mg. in C_1).

The oxime was recrystallized from ethanol–water; m.p. 89.5–90° (1.31 mμc./mg. C; 7.86 mμc./mg. in C_1).

The semicarbazone was recrystallized from ethanol–water; m.p. 165–166° (1.11 mμc./mg. C; 7.77 mμc./mg. in C_1).

The 2,4-dinitrophenylhydrazone was crystallized from ethanol; m.p. 159.5–160° (0.66 mμc./mg. C; 7.92 mμc./mg. in C_1).

Degradation of Cyclohexanone-1-C^{14}.—Following Smith,[29] 0.25 g. of sodium azide was added to an ice-cold solution of 0.25 g. of cyclohexanone-1-C^{14} in 1.25 ml. of concentrated hydrochloric acid. After 12 hr. at room temperature, the solution was heated at 100° for 4 hr. Evaporation of the solvent in a stream of nitrogen and drying *in vacuo* left a solid which was leached with 5 ml. of absolute ethanol. The ethanolic filtrate was concentrated and dried giving 0.29 g. of crude amino acid hydrochloride.

A solution of this material in 1 ml. of concentrated sulfuric acid was kept *in vacuo* to remove hydrogen chloride, cooled to 0° and treated with 0.195 g. of sodium azide. The solution was heated to 40° for 2 hr. and 60° for 1.5 hr., diluted with water, made strongly alkaline with sodium hydroxide and shaken with 0.36 g. of benzoyl chloride in 5 ml. of chloroform. Concentration of the chloroform solution yielded a solid which was washed with water, dried and crystallized from ethanol–water to give 0.21 g. of the dibenzamide of pentamethylene diamine, m.p. 131.5–132.5° (reported[30] m.p. 132–133°) (radioactivity indistinguishable from background).

Cycloheptanone-1-C^{14}.—In a 500-ml., three-necked, round-bottom flask equipped with stirrer and thermometer, a mixture of 98.6 g. (1.005 mole) of cyclohexanone-1-C^{14} (1.30 mμc./mg. C), 75 ml. of methanol and 147.5 ml. of 30% aqueous sodium hydroxide was cooled to −10° and treated with 85 g. (0.825 mole) of N-methyl-N-nitrosourea in portions of 4–5 g. at 10-min. intervals with stirring, the temperature being maintained at −10°. The mixture was stirred and allowed to come to room temperature overnight and filtered. The filter cake was washed with ether. The filtrate was extracted with three 100-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate and concentrated. Fractional distillation afforded 44 g. (48% of the theoretical yield based on urea used) of cycloheptanone-1-C^{14}; b.p. 108–111° at 110 mm., $n^{26}D$ 1.4578 (1.11 mμc./mg. C; 7.77 mμc./mg. in C_1).

The 2,4-dinitrophenylhydrazone was crystallized from ethanol; m.p. 146–147° (0.62 mμc./mg. C; 8.06 mμc./mg. in C_1).

2,4,7-Tribromotropone-1-C^{14}.—This material was prepared from 28.0 g. of cycloheptanone-1-C^{14} (1.11 mμc./mg. C) according to the procedure of Doering and Sayigh.[6] The crude, dried tribromocycloheptanone, obtained in quantitative yield, was used directly in the next step. The three bromination-heating steps applied to 88.2 g. of crude tribromocycloheptanone in 250 ml. of acetic acid involved (a) 120 g. of bromine in 300 ml. of acetic acid, (b) 78 g. of bromine, and (c) 40 g. of bromine. The combined crops of tribromotropone were crystallized from methanol yielding 28.7 g. (33.6% of theory based on cycloheptanone); m.p. 183.5–184.5° (reported[6] 184.5–185.5°) (1.13$_5$ mμc./mg. C; 7.94 mμc./mg. in C_1).

Tropone-1-C^{14}.—In 80 ml. of absolute ethanol, 2.0 g. of palladium hydroxide (5% on barium sulfate) was hydrogenated in 40 min., 25 ml. of hydrogen being absorbed. There was now added 0.012 g. of thiourea in 10 ml. of ethanol, 4.0 g. of potassium acetate and 2.0 g. (0.00583 mole) of 2,4,7-tribromotropone-1-C^{14} (1.13 mμc./mg. C). At atmospheric pressure and room temperature, 418 ml. of hydrogen was absorbed in 43 min. to complete the hydrogenation. The filtered catalyst was washed with a few ml. of ethanol.

The ethanolic solutions from three such runs were united, concentrated to *ca.* 25 ml. at room temperature *in vacuo*, diluted with 20 ml. of water, neutralized with solid sodium bicarbonate and extracted continuously with ether for 10 hr. The ether extract was dried over magnesium sulfate and concentrated at room temperature to a residue, two successive evaporative distillations of which, at 25° and 0.05 mm., afforded 0.38 g. (20% of theory) of tropone-1-C^{14}; $n^{23}D$ 1.5948. The infrared spectrum indicated contamination by cycloheptanone.

2,7-Dibromotropone-1-C^{14}.—To a solution of 0.21 g. (0.0020 mole) of tropone-1-C^{14} in 8 ml. of acetic acid, there was added a solution of 0.64 g. (0.0040 mole) of bromine in 4 ml. of acetic acid. After standing 12 hr. at room temperature, the solution was evaporated to dryness in a stream of nitrogen. The residue was triturated with 5 ml. of 10% aqueous sodium bicarbonate solution and extracted with 5 ml. of chloroform. The chloroform extract was washed with 2 ml. of water, dried over magnesium sulfate and evaporated to a residue of 0.41 g. which was crystallized twice from methanol to give 0.0536 g. (10%) of 2,7-dibromotropone-1-C^{14}, m.p. 169–170° (reported[31] 170–171°).

A mixture of 0.0536 g. of 2,7-dibromotropone-1-C^{14} and 0.1792 g. of inactive 2,7-dibromotropone was homogenized by dissolving in acetone and evaporating to dryness. This material, calculated to have 0.26 mμc./mg. C, was found to have 0.26 mμc./mg. C (1.82 mμc./mg. in C_1).

***o*-Bromobenzoic Acid-carboxyl-C^{14}.**—A suspension of 0.2067 g. (0.784 mmole) of 2,7-dibromotropone-1-C^{14} (0.26 mμc./mg. C) in 5 ml. of 1 *N* aqueous sodium hydroxide was heated 15 min. on the steam-bath and allowed to stand 45 min. at room temperature. Acidification with 6 *N* hydrochloric acid and centrifuging afforded product which was washed with water, dried *in vacuo* over calcium chloride, sublimed and crystallized to yield 0.067 g. (43% of theory) of *o*-bromobenzoic acid-carboxyl-C^{14}, m.p. 147.5–148° (0.256 mμc./mg. C; 1.79 mμc./mg. in C_α).

Degradation of *o*-Bromobenzoic Acid-carboxyl-C^{14}.—To 0.0568 g. (0.000283 mole) of *o*-bromobenzoic acid-carboxyl-C^{14} in 0.5 ml. of concentrated sulfuric acid, 0.020 g. (0.000307 mole) of sodium azide was added at 0°. Attached to a Phares apparatus[32] and isolated as described below, the reaction yielded barium carbonate (1.77 mμc./mg. C).

The acidic solution was diluted with 5 ml. of water, made alkaline and treated with 0.05 g. of benzoyl chloride as described below to yield 0.014 g. of benz-*o*-bromoanilide, m.p. 107–108° after one crystallization from hexane. This material was diluted with 0.020 g. of inactive benz-*o*-bromoanilide and recrystallized to give 0.0261 g. of benz-*o*-bromoanilide, m.p. 112–113° (radioactivity indistinguishable from back-

(25) T. Nozoe, Y. Kitahara, K. Yamane and K. Yamaki, THIS JOURNAL, **26**, 14 (1950).

(26) J. W. Cook, J. D. Loudon and D. K. V. Steel, *J. Chem. Soc.*, 530 (1954).

(27) R. Christian Anderson, Y. Delabarre and A. A. Bothner-By, *Anal. Chem.*, **24**, 1298 (1952).

(28) This material, a most generous gift, had been synthesized by Drs. R. Christian Anderson and D. R. Christman of the Brookhaven National Laboratory from radioactive carbon dioxide and the bis-Grignard reagent from pentamethylene bromide.

(29) P. A. S. Smith, THIS JOURNAL, **70**, 320 (1948).

(30) J. v. Braun and W. Pinkernelle, *Ber.*, **67**, 1056 (1934).

(31) T. Nozoe, S. Seto and S. Matsumura, *Proc. Japan Acad.*, **28**, 483 (1952).

(32) E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).

ground). The material from the mother liquor likewise showed no detectable radioactivity.

2,4- and 2,5-Dibromobenzoic Acids-carboxyl-C^{14}.—A mixture of 2.0 g. (0.00583 mole) of 2,4,7-tribromotropone-1-C^{14}, 0.82 g. of sodium hydroxide and 10 ml. each of water and ethanol was swirled for 15 min., heated 30 min. on the steam-bath and then concentrated to half its volume on the steam-bath by blowing with a stream of nitrogen. The mixture was cooled, acidified with 6 *N* hydrochloric acid and filtered. The product was washed with water, dried *in vacuo* over calcium chloride and sublimed at 130° and 1 mm. to yield 1.46 g. (89.6% of theory) of the mixed dibromobenzoic acids, m.p. 110–125° (1.12_5 mμc./mg. C; 7.88 mμc./mg. in Cα).

Benzoic Acid-carboxyl-C^{14}.—A mixture of 1.41 g. (0.00504 mole) of the mixed dibromobenzoic acids, 0.82 g. (0.01 mole) of sodium acetate, 0.10 g. of 10% palladium-on-charcoal catalyst and 10 ml. of ethanol was hydrogenated at atmospheric pressure, the reaction being complete in 3 hr. and 279 ml. of hydrogen being absorbed. The filtered reaction mixture was concentrated, treated with 3 ml. of 2 *N* hydrochloric acid and extracted with two 10-ml. portions of ether. Evaporation of the ether left a residue which was dried *in vacuo* and crystallized from cyclohexane giving 0.35 g. (57% of theory) of benzoic acid-carboxyl-C^{14}, m.p. 121–122° (1.13_5 mμc./mg. C; 7.94 mμc./mg. in C_α).

Degradation of Benzoic Acid-carboxyl-C^{14}.—To a solution of 0.122 g. (0.00100 mole) of benzoic acid-carboxyl-C^{14} (1.13 mμc./mg. C) in 1 ml. of concentrated sulfuric acid cooled to 0°, there was added 0.08 g. (0.00123 mole) of sodium azide. The flask was immediately attached to a Phares apparatus,[32] which contained 10 ml. of 1 *N* sodium hydroxide solution. The mixture was heated for 2 hr. at 40°, and then nitrogen was bubbled through for 30 min. The sodium hydroxide solution was then poured into a solution of 0.50 g. of barium chloride in 10 ml. of water. The barium carbonate was filtered under nitrogen, washed successively with water, 1:1 water–methanol and then dried at 100°, 0.176 g. (89.3% of theory) (8.08 mμc./mg. C).

The acidic solution was cooled to 0°, diluted to 7 ml. with water, made alkaline with concentrated aqueous sodium hydroxide solution and shaken for 10 min. with 0.16 g. (0.00114 mole) of benzoyl chloride in 5 ml. of chloroform. Separation and concentration *in vacuo* of the chloroform solution left a crystalline mass which was washed with water and dried *in vacuo* over calcium chloride. Two crystallizations from ethanol–water afforded 0.13 g. (66% of theory) of benzanilide, m.p. 161.5–162.5° (radioactivity indistinguishable from background).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Anthochlor Pigments. X. Aureusin and Cernuoside

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Aureusin and cernuoside, glucosides of 3′,4′,4,6-trihydroxyaurone (aureusidin) have been shown to be the 6- and 4-glucoside, respectively.

The orange-yellow pigment aureusidin (I or II, R = R′ = H) was first isolated in the form of the heptaacetate of its glucoside, aureusin, from a yellow variety of the garden snapdragon, *Antirrhinum majus*.[1] It was subsequently found to be present in the flowers of all of the non-albino color forms of the same plant, in amounts controlled by a single genetic factor.[2] Aureusin and other aureusidin glycosides have also been found to occur in a number of other flowers.[3] In particular, *Oxalis cernua* L. contains aureusin and, in larger amounts, another aureusidin glucoside, cernuoside.[3–5] Cernuoside is clearly distinguished from aureusin by its different rate of movement on paper chromatograms. Since both pigments are monoglucosides of aureusidin[1,4] the establishment of the point of attachment of the sugar residue in each of the two pigments would determine their complete structures.

Complete methylation of the two glucosides, followed by acid hydrolysis, yielded the two monohydroxy-trimethoxyaurones. The glucosides, their methyl ethers and the partially methylated aglucones were examined by spectrophotometric and chromatographic methods. Particular use was made of the fact that the spectra only of aurones[6] bearing a 4-hydroxyl group are shifted by the addition of aluminum chloride.[7] The spectral shifts brought about by the addition of alkali gave further information, and are discussed below.

The spectra of aureusin, which was prepared for the first time by the mild alkaline hydrolysis of its heptaacetate,[8] showed that the sugar was not in either position 4 (since the long wave length maximum was shifted bathochromically 60 mμ by aluminum chloride) or 4′ (since there was an 85 mμ shift in alkali). Methylation of aureusin, followed by removal of the sugar residue, gave a product which was spectrally and chromatographically identical with an authentic sample of 6-hydroxy-4,3′,4′-trimethoxyaurone (I, R = H, R′ = Me) and different from the isomeric compounds, 4′-hydroxy-4,6,3′-trimethoxyaurone (III, R = OMe) and 3′-hydroxy-4,6,4′-trimethoxyaurone (IV, R = OMe). The three synthetic aurones were prepared by the condensation of the appropriate coumaranone[9] with veratraldehyde, vanillin and isovanillin, respectively.

The spectrum of cernuoside was not altered by the addition of aluminum chloride solution, an indication that the compound is the 4-glucoside of aureusidin (II, R = glucosyl, R′ = H). This was confirmed by the methylation of cernuoside,[10] followed by acid hydrolysis. The ultraviolet spec-

(1) M. K. Seikel and T. A. Geissman, THIS JOURNAL, **72**, 5725 (1950).

(2) T. A. Geissman, E. C. Jorgensen and B. L. Johnson, *Arch. Biochem. Biophys.*, **49**, 368 (1954).

(3) E. C. Jorgensen, Ph.D. Thesis, University of California, Los Angeles, 1953.

(4) A. Ballio, S. Dittrich and G. B. Marini-Bettolo, *Gazz. chim. ital.*, **83**, 224 (1953).

(5) R. Lamonica and G. B. Marini-Bettolo, *Ann. Chim.*, **42**, 496 (1952).

(6) E. C. Bate-Smith and T. A. Geissman, *Nature*, **167**, 688 (1951).

(7) J. B. Harborne, *Chemistry and Industry*, 1142 (1954).

(8) A sample was kindly furnished by Dr. M. K. Seikel.

(9) T. A. Geissman and E. H. Hinreiner, THIS JOURNAL, **73**, 785 (1951); E. H. Hinreiner, Ph.D. Thesis, University of California, Los Angeles, 1951.

(10) A sample of cernuoside from *Oxalis cernua* was kindly furnished by Dr. Marini-Bettolo.