[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND WELLESLEY COLLEGE]

The Chemistry of Flower Pigmentation in *Antirrhinum majus*. V.[1] Pigments of Yellow *Antirrhinum majus*,[2,3] Genotype ppmmyy[4]

BY MARGARET K. SEIKEL

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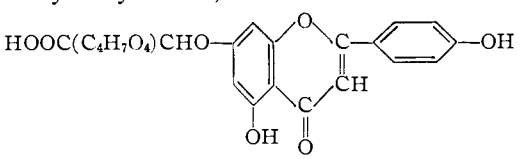
From the pure genotype ppmmyy of *Antirrhinum majus* the single flavone pigment apigenin-7-glucuronide has been isolated as its acetate. The glycosidic naringenin pigment in this species has been shown to be a 7-glucoside.

Work on the correlation of the genetics and the flower pigments of *Antirrhinum majus* was initiated by a study of the triply recessive yellow genotype, ppmmyy.[4] In the earlier research[2] on the yellow petals of mixed genotypes the yellow pigment aureusin had been identified as a glucoside of 3′,4′,4,6-tetrahydroxybenzalcoumaranone, and a hexoside of the flavanone pigment naringenin (4′,5,7-trihydroxyflavanone) had been isolated in addition. Although large amounts of flavone pigments were also encountered in this work, it had not been possible to isolate and purify them in the form of their acetates or of the acetates of their aglucones, evidently because of the presence of more than one pigment of this class.[3] When, however, the pure genotype ppmmyy was studied by the same methods, the acetate of the flavone pigment was purified readily. This compound (I) was identified as the pentaacetate of II, the 7-glucuronide of apigenin (4′,5,7-trihydroxyflavone).



II, apigenin-7-glucuronide

The presence of apigenin in yellow *Antirrhinum majus* had been reported earlier by Wheldale and Bassett[5] and the recent paper chromatographic work of Geissman and co-workers[3] showed that apigenin is the only flavone in this genotype.

The flavone pigment was differentiated from the aurone[6] pigment by the yellow colors it produced with base and with concentrated acid and from the flavanone pigment by the pink-orange shades it yielded with magnesium and hydrochloric acid. Also, the spectrum of its pentaacetate was quite different from the spectra of the acetates of these other types of pigments (compare Table I with the data given in reference 2), but closely resembled those of acetoxyflavones reported by Skarzynski[7] and those of apigenin triacetate and luteolin tetraacetate described in this paper (Table I). It was shown to be a glycoside by hydrolysis of its pure acetate; this procedure yielded a solution giving a Molisch test and a flavone which formed a new acetate. This acetate was identified as apigenin triacetate (III) by a mixed melting point and by a comparison of absorption spectra (Table I).

From this genotype of *Antirrhinum majus*, aureusin was also isolated in the form of its acetate IV, but the naringenin pigment was present in too small quantities to obtain a pure sample of its acetate V.

Paper chromatography was employed to identify the sugars present in the three pigments so far isolated from yellow *Antirrhinum majus*. Earlier work[2] had pointed to the presence of glucose in aureusin and a hexose[8] in the flavanone pigment, but the analytical results from I did not agree with the values calculated for a simple hexose. By paper chromatography the presence of glucose in aureusin was verified and the hexose attached to naringenin was also shown to be glucose. The sugar linked to apigenin was found to be glucuronic acid, readily identified by the two characteristic spots, pink or rose in color, when a spray of *m*-phenylenediamine dihydrochloride was used,[9] the slower moving one being heart-shaped[10] and the faster moving one being less distinct. The latter is caused by the presence of the lactone which differentiates glucuronic from galacturonic acid.[10] Glucuronic acid has been found only rarely among the flavonoid glycosides; Marsh[11] lists three such glucuronides while querciturон, a quercetin glucuronide, is also known[12] and apigenin-7-glucuronide was reported recently.[13]

The position of the sugars in the three glycosidic pigments isolated from *A. majus* has now been shown to be in the B ring, *para* to the carbonyl. Harborne and Geissman[14] recently have identified aureusin as the 6-glucoside of 3′,4′,4,6-tetrahydroxybenzalacoumaranone. In the present work the apigenin glucuronide pentaacetate (I) was deacetylated–methylated and hydrolyzed and the product shown to be the 4′,5-dimethyl ether of apigenin (VI) by a comparison of the spectral data with the very distinctive spectral data recorded for the three iso-

(1) For the preceding paper in this series see T. A. Geissman and J. B. Harborne, *Arch. Biochem. and Biophys.*, **55**, 447 (1955).

(2) For previous work see M. K. Seikel and T. A. Geissman, THIS JOURNAL, **72**, 5725 (1950).

(3) For related work see T. A. Geissman, E. C. Jorgensen and B. L. Johnson, *Arch. Biochem. and Biophys.*, **49**, 368 (1954), and E. C. Jorgensen and T. A. Geissman, *ibid.*, **54**, 72 (1955).

(4) The plant material was grown by B. L. Johnson of the Department of Ornamental Horticulture of the University of California at Los Angeles.

(5) M. Wheldale, *Biochem. J.*, **7**, 87 (1913); *J. Genetics*, **4**, 109 (1914); M. Wheldale and H. L. Bassett, *Biochem. J.*, 441 (1913); *Proc. Roy. Soc. (London)*, **87B**, 300 (1914).

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

(7) B. Skarzynski, *Biochem. Z.*, **301**, 150–169 (1939).

(8) By analysis only.

(9) M. K. Seikel, A. L. Haines and H. D. Thomson, THIS JOURNAL, **77**, 1199 (1955).

(10) S. M. Partridge, *Biochem. J.*, **42**, 243 (1948).

(11) C. A. Marsh, *ibid.*, **59**, 58 (1955).

(12) G. Endres, R. Hüttel and L. Kaufmann, *Ann.*, **537**, 206 (1939).

(13) K. Imai and T. Mayama, *J. Pharm. Soc. Japan*, **73**, 128 (1953); *C. A.*, **47**, 12370 (1953).

(14) J. B. Harborne and T. A. Geissman, THIS JOURNAL, **77**, 4622 (1955).

TABLE I

DATA ON ABSORPTION SPECTRA[a]

Compound	Band I λmax, mμ	log ε	λmin, mμ	log ε	Band II λmax, mμ	log ε	λmin, mμ	log ε
Apigenin glucuronide pentaacetate (I)[c]	302	4.44	269	4.07	257	4.33	240	4.24
Apigenin triacetate (III) natural[c]	298.5	4.38	270	3.98	255	4.27	236	4.05
III, synthetic[b]	299	4.39	270	4.00	256	4.29	236	4.09
Luteolin tetraacetate synthetic[b]	300	4.35	270	4.04	258	4.30	238	4.14

[a] Determined with Beckman quartz spectrophotometers, model DU. [b] In 95% alcohol. [c] In absolute alcohol.

meric dimethyl ethers of apigenin by Nordström and Swain.[15] Therefore compound I is the acetate of the 7-glucuronide of apigenin and II is identical with the glucuronide recently isolated from the compositae *Erigeron annus*.[13] Naringenin glucoside acetate (V)[2] was hydrolyzed by weak alkali to the free glucoside which was shown by spectral data and chromatography to be identical with naringenin 7-glucoside (VII) obtained by partial hydrolysis of naringin (naringenin 7-rhamnoglucoside). This partial hydrolysis and separation was carried out much more simply than that recently reported by Fox, Savage and Wender.[16] The acetyl derivative of the 7-glucoside from naringin was also identical with the original acetate. The glucoside of naringenin from *A. majus* is thus identical with the prunin obtained from *Prunus yedoensis*.[17]

Experimental[18]

Extraction of Plant Material.—Yellow blossoms of the triply recessive genotype ppmmyy of *Antirrhinum majus* derived from the cross between the yellow "Ball Gold" (ppMMyy) and the pink "Cheviot 33" (PPmmYY) were used for this work. They were prepared and extracted as previously described for yellow petals of mixed genotypes.[2]

Aureusin Heptaacetate (IV).—The benzalcoumaranone pigment was isolated and acetylated as before.[2] The acetylated product was purified by extraction as previously described for large amounts[2] and recrystallized twice from ethyl acetate. From 75 g. of petals 0.080 g., m.p. 264.5–266°, was obtained. It was identified as IV by color tests (rose-red with 10% sodium hydroxide, vivid orange-red with concentrated sulfuric acid) and by a mixed melting point of 262–263° with material previously isolated from miscellaneous genotypes (authentic material, m.p. 261.5–262.5°).

Attempts to Isolate Naringenin 7-Glucoside Hexaacetate (V).—No pure sample of V could be obtained by the method previously described or by slight variations of this method. The failure undoubtedly was caused by too small amounts since the earlier isolation of this compound had been done on runs employing 1 lb. instead of 60 g. of dry petals. That a flavanone was present was indicated by the yellow precipitate obtained with basic lead acetate and by the isolation of a trace of white crystalline acetyl derivative, m.p. 186.5–188.5° (authentic V melts at 195.5–197°), which gave a deep bluish-pink color in the ethanol–magnesium–hydrochloric acid test and yellow with base and concentrated sulfuric acid.

Apigenin 7-Glucuronide Pentaacetate (I).—The methanolic solutions from which crude IV had crystallized were allowed to stand and evaporate slowly. If gums settled out, the solutions were rediluted and allowed to stand. Crystals were obtained after periods varying from a day to a week or two and further crops were isolated by similar treatment of the filtrates. By color tests with sodium hydroxide and concentrated sulfuric acid the various crops were easily recognized as benzalcoumaranone acetate (red colors with both), and impure flavone acetate (yellow colors mixed with varying amounts of red). Little could be deduced from the melting points, which were in the range 220–250°. From the total crude acetylated pigments approximately 20% was obtained in crystalline form, of which more than half was flavone acetate. Once crystallized, compound I was separated easily from traces of IV by extraction with hot methanol or recrystallization from acetone, the latter staying in solution. In these ways 0.4–0.5 g. of I giving pure lemon-yellow colors with base and acid and melting in the region 220–230°, was obtained from 60–75 g. of dry petals.

Compound I was further purified by recrystallization from large volumes of ethanol (0.1 g. in *ca.* 150 ml.), the recovery averaging 90%, or from similarly large volumes of acetone which had to be evaporated to one-third before compound I reprecipitated in 85% recovery. It crystallized from both solvents in a fibrous mat which under the microscope appeared as long, silky, colorless hairs. When plunged into a bath preheated to 220°, compound I melted at 224–224.5°. In the ethanol–magnesium–hydrochloric acid test it gave a pink-orange color after preliminary heating with hydrochloric acid to hydrolyze the acetyl groups. Other color tests are mentioned above.

Anal. Calcd. for $C_{31}H_{28}O_{16}$: C, 56.71; H, 4.30. Found: C, 56.69; H, 4.81.

Apigenin Triacetate (III).—A 0.1-g. sample of I was hydrolyzed quantitatively to its aglucone with 0.6 *N* hydrochloric acid by the method previously described for the hydrolysis of IV.[2] The crude, mustard-tan aglucone melted at 348–350° (recorded for apigenin, 347°,[19] 347–348°[20]). This was acetylated by the usual method[2] and the acetate recrystallized three times from methanol. The acetate was identified as apigenin triacetate, m.p. 181–182°,[21] by a mixed melting point with an authentic sample (unknown, mixed and authentic, 181–182.5°), by analysis, by a comparison of its absorption spectrum with that of an authentic sample (Table I) and by color tests matching those given by the authentic sample (10% sodium hydroxide, lemon-yellow appearing slowly; concentrated sulfuric acid, vivid green-yellow; ethanol–magnesium–hydrochloric acid after preliminary hydrolysis with concentrated acid, flesh tones becoming yellow with excess acid).

Anal. Calcd. for $C_{21}H_{16}O_8$: C, 63.64; H, 4.07. Found: C, 63.76; H, 3.93.

Identification of Sugars by Paper Chromatography.—Solutions[22] of sugars from the acidic hydrolysis of the crystalline acetates of the pigments were freed from hydrogen ion and chloride ion as described before.[2] The filtrates were concentrated *in vacuo* with slight heating to a volume calculated to contain 1% of a hexose. Small amounts of black free silver were removed, but more was deposited very slowly as the solutions stood. The unknown sugar solutions and authentic solutions of various sugars were chromatographed and sprayed as described before.[9] The results are shown in Table II.

Conversion of Apigenin Glucuronide Pentaacetate (I) to Apigenin 4′,5-Dimethyl Ether (VI).—Two milligrams of I was subjected to deacetylation–methylation[2] by dissolving it in 3 ml. of warm methanol and to the warm solution adding alternately, with stirring, micro drops of 50% potassium hydroxide and dimethyl sulfate. After a total of 0.75 ml. of the former and 0.4 ml. of the latter had been added, the yellow color formerly appearing whenever the solution was basic no longer developed. The cooled basic solution was

(15) C. G. Nordström and T. Swain, *J. Chem. Soc.*, 2764 (1953).

(16) D. W. Fox, W. L. Savage and S. H. Wender, THIS JOURNAL, **75**, 2504 (1953).

(17) M. Hasegawa and T. Shirato, *ibid.*, **74**, 6114 (1952).

(18) All melting points are uncorrected.

(19) "Beilstein," Vol. 18, 1934, p. 182.

(20) F. Mayer and A. H. Cook, "The Chemistry of Natural Coloring Matters," Reinhold Publ. Corp., New York, N. Y., 1943, p. 172.

(21) "Beilstein," Vol. 18, 1934, p. 183.

(22) The solutions were 1–2.5 years old when this work was done, and all but one still chromatographed successfully 1.5 years later.

TABLE II

IDENTIFICATION OF SUGARS

Source of sugar: Genotype	Pigment	R_f	Color of spot	Identity of sugar
Misc. yellow[a]	Aureusin	0.19	Tan-yellow	Glucose[b]
Misc. yellow[a]	Naringenin glycoside	.20	Orange-yellow	Glucose
ppmmyy	Apigenin glycoside	.14[c]	Pink[d]	Glucuronic acid[e]
		.38		
Authentic sugars:	Glucose	.20	Orange-yellow	
	Glucuronic acid	.13[c]	Orange-pink	
		.37		

[a] Solution obtained in work reported in reference 2. [b] Previously identified by analysis and formation of glucosazone. Here clearly differentiated from fructose (R_f 0.25) and mannose (R_f 0.24). [c] From the M.A. thesis of Harriet D. Thompson, Wellesley College, 1953. [d] Only faint spots so shade of pink not discernible. [e] Clearly differentiated from galacturonic acid since the latter gave only one pink spot, R_f 0.15, reference 9.

diluted with water to 5 ml. and extracted with ether, a non-acidic flavonoid impurity being removed. The *p*H was then reduced to 2 with hydrochloric acid, the solution saturated with sodium chloride and the methylated apigenin glucuronide extracted slowly with large volumes of ether and chloroform. The yellow residue which was obtained from evaporation of the extracts and which gave a yellow color with concd. sulfuric acid was hydrolyzed as prescribed by Nordström and Swain.[15] The trace of apigenin dimethyl ether obtained was identified as the 4′,5-isomer by the data given in Table III.

TABLE III

DETERMINATION OF THE POSITION OF GLUCURONIC ACID IN APIGENIN GLUCURONIDE PENTAACETATE (I)

	Apigenin 4′,5-dimethyl ether: Found	Authentic[a]
Colors on paper		
in ultraviolet	Light blue	Very pale blue
in ultraviolet plus NH_3	Light yell.	Yellow
R_f[b]		
Butanol–acetic acid–water[c]	0.91	
30% acetic acid (v./v.)	.41	
Butanol–water	.82	
Butanol–water on borate paper,		
*p*H 8.7[d]	.77[d]	[e]
*p*H 10.0 (0.1 *M* $NaBO_2$)	.30[f]	
λ_{max}, mμ[g]		
95% alcohol, Band I	326	325
Band II	265[i]	260
Plus $NaOC_2H_5$,[h] Band I	358	360
Band II	274	272
$\triangle$D (%)[a] with		
$NaOC_2H_5$, Band I	−32	−32
Band II	+58[i]	+70
Plus $AlCl_3$[i]	No shift in spectrum	

[a] Reference 15. [b] On Whatman No. 1, not equilibrated with solvents; leading edge of spots measured. [c] Equal volumes of *n*-butyl alcohol and 27% acetic acid; see reference 3. [d] Prepared according to C. A. Wachtmeister, *Acta Chem. Scand.*, **5**, 976 (1951); apigenin, R_f 0.85, apigenin trimethyl ether, 0.81. [e] R_f 0.51 with no *p*H specified; reference 15 and T. Swain, *Biochem. J.*, **53**, 200 (1953). [f] Apigenin, 0.16, apigenin trimethyl ether, 0.81. [g] Determined with a Beckman quartz spectrophotometer, model DU. [h] Three drops of 0.1 *M* sodium ethylate added to the 3 ml. of solution in the quartz cell and to the reference solution. [i] Three drops of aluminum chloride (5% in alcohol) added likewise. [j] Divergences of this band probably caused by the use of pure 95% alcohol as a reference solution instead of a reaction blank as in reference 15.

Naringenin 7-Glucoside (VII) from Naringenin Glucoside Hexaacetate (V).—Two milligrams of V, m.p. 195.5–197°, obtained from yellow *Antirrhinum majus* of miscellaneous genotype, was treated with a mixture of 0.7 ml. of saturated barium hydroxide and 0.3 ml. of water in an atmosphere of nitrogen. After 40 hours with occasional shaking the precipitate had completely dissolved. The yellow solution was acidified to *p*H 3, but no color change occurred. The acidic solution then was warmed for 15 min. on a steam-bath. This caused considerable decrease in the yellow color and accompanying increase in the pink color obtained in the ethanol–magnesium–hydrochloric acid test; the chalcone isomer was thus removed from the equilibrium mixture. The cooled mixture was then extracted with ether to remove any naringenin, then saturated with salt and extracted many times with ether. The trace of residue obtained from these last extractions was identified as VII by a comparison of the properties listed in Table IV with those of authentic VII from naringin.

Naringenin 7-Glucoside (VII) from Naringin.—Naringin was partially hydrolyzed by refluxing a solution of 0.5 g. in 50 ml. of methanol and 50 ml. of 2 *N* hydrochloric acid for 1.5–2 hours. Paper chromatography showed that in this length of time the naringin spot had almost disappeared, the naringenin spot was still weak, but that the spot of intermediate R_f, presumably VII, was by far the most prominent. VII was isolated for study in two ways. Small amounts of hydrolysate could be banded directly on Whatman No. 3 paper, developed by either butanol–acetic acid–water[23] or 5% acetic acid and the central band, fluorescing white by ultraviolet light, cut out and eluted with methanol. With larger amounts the methanol was removed from the reaction mixture by evaporation *in vacuo* and the residual aqueous solution was extracted first with small volumes of ether, which was then washed with water. The ether extract was shown by chromatography to contain all the naringenin and some of VII. Extraction of the aqueous layer and washings (saturated with salt) with propanol removed the main body of VII plus traces of residual naringin. After evaporation of the propanol and solution of the residue in

TABLE IV

PROPERTIES OF NARINGENIN 7-GLUCOSIDE (VII)

	From *A. majus*	From naringin	Mixture
M.p., °C.[a]		221–223	
M.p. acetate, °C.[a]	192.5–194[b]	192–192.5	192.5–194
R_f 5% acetic acid	0.56	0.56	0.56
R_f 3% NaCl	.38	.38	.38
R_f BAW[c]	.78	.78	.78
R_f 30% acetic acid	.79	.79	.79
R_f 60% acetic acid[d]	.76	.74	.76
λmax, mμ			
95% alcohol, Band I	284[e]	285[e,f]	
Band II	*ca.* 227	225	
Plus $AlCl_3$,[g] Band I	304[h]	306[h]	
Band II		225	
Plus $NaOC_2H_5$,[g] Band 1	*ca.* 266[i]	*ca.* 270[i]	

[a] Uncorrected. [b] Recorded in reference 2, 195.5–197°. [c] Footnote 23. [d] Recorded 0.84, reference 16. [e] Recorded for prunin, 283 mμ, reference 17. [f] Also a low barely differentiated maximum at 329 mμ which with $AlCl_3$ gives a well-differentiated maximum at 382 mμ; this region was not studied with the other sample. [g] See Table III, footnotes *h* and *i*. [h] Shift without change in intensity. [i] Extremely unstable because of formation of the chalcone in basic solution.

(23) Equal volumes of *n*-butyl alcohol and 27% acetic acid.

methanol or absolute ethanol, crystals of VII separated slowly. Over a period of two weeks 0.121 g. was obtained and shown by chromatography to be pure or almost pure VII. After recrystallization from methanol, from which it separated slowly, and dissolvation at 165–175°, it melted at 221–223° (recorded 225°[16,17]). It resembled naringin and naringenin in giving bright yellow colors with base and strong acid and a purplish-brown with ferric chloride; with ethanol, magnesium and hydrochloric acid it produced a fuschia (red-purple) color like naringin but different from the orange-red of naringenin.

The acetyl derivative of VII was prepared by boiling the 29 mg. of amorphous tan powder isolated from banding on paper for two minutes with excess acetic anhydride and sodium acetate.[24] After several recrystallizations from methanol it did not depress the melting point of V from *A. majus* (see Table IV).

(24) This acetylation was very unreliable in producing a crystalline product.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, UNIVERSITY OF MICHIGAN AND TULANE UNIVERSITY]

The Transformation of ψ-*o*-Dinitroso Aromatic Compounds into *o*-Nitroaryl Amines[1]

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ψ-*o*-Dinitrosobenzene and 4-methyl-ψ-*o*-dinitrosobenzene were quantitatively transformed by copper in hydrochloric acid into *o*-nitroaniline and a mixture of 3-nitro-4-aminotoluene (39.0%) and 3-amino-4-nitrotoluene (61.0%), respectively. *o*-Benzoquinone dioxime was isomerized by copper in hydrochloric acid, by cuprous chloride and by cupric chloride into *o*-nitroaniline. The treatment of ψ-1,2-dinitrosonaphthalene with copper in hydrochloric acid brought about the formation of nitronaphthylamines in trace amounts and a stable copper chelate. Naphthofurazan was obtained from the chelate. Attempts to oxidize 9,10-phenanthrenequinone dioxime into 9,10-ψ-dinitrosophenanthrene were unsuccessful.

Introduction

An unsymmetrical furoxane structure for the N_2O_2 moiety attached through nitrogen atoms to *o*-positions of an aromatic nucleus has not proved to be satisfactory.[3] Renaming "furoxanes" of this type as ψ-*o*-dinitrosoaromatic compounds and adopting the use of a hybrid structure, *cf.* I, is proposed.[4]

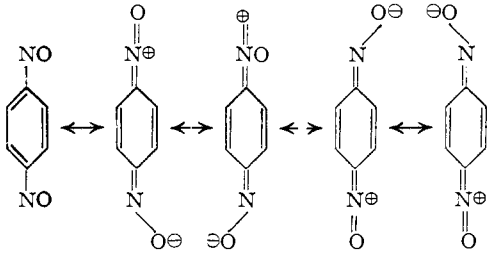
(1) The financial support for this work was provided by O. O. R. under contract Nos. DA-20-018-ORD-11814 and DA-01-009-ORD-331. Purchase of the Fisher Elecdropode represents partial use of funds obtained from the Research Corporation. The work was presented in part at the combined Southeast and Southwest Region Meeting, A. C. S., New Orleans, La., December, 1953.

(2) Department of Chemistry, Tulane University, New Orleans, La.

(3) (a) M. O. Forster and M. F. Barker, *J. Chem. Soc.*, **103**, 1918 (1913); (b) D. L. Hammick, W. A. M. Edwardes and E. R. Steiner, *ibid.*, 3308 (1931); J. H. Boyer, D. I. McCane, W. J. McCarville and A. T. Tweedie, THIS JOURNAL, **75**, 5298 (1953).

(4) The deficiencies of those structures which represent true nitroso compounds, cyclic dioxime peroxides and those which require a four-membered ring of alternating nitrogen and oxygen atoms have been demonstrated.[3b]

Whereas *m*-dinitrosobenzene is a true nitroso compound, the *p*-isomer is not (T. W. J. Taylor and W. Baker, Sidwick's "Organic Chemistry of Nitrogen," Oxford University Press, London, 1945 (corrected), p. 213). A similar hybrid structure for ψ-*p*-dinitrosobenzene is in agreement with the paucity of information which describes properties of the molecule[3a] (R. Nietzki and F. Kehrmann, *Ber.*, **20**, 613 (1887); see reference 14).



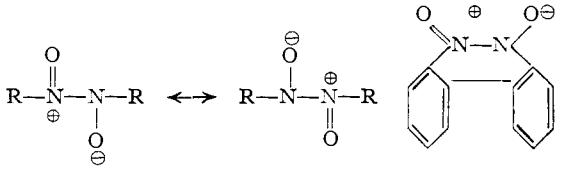
These hybrid structures for ψ-dinitroso aromatic compounds are analogs of C-nitroso dimers (C. P. Fenimore, THIS JOURNAL, **72**, 3226 (1950)) and 2,2-dinitrosobiphenyl (S. D. Ross and I. Kuntz, *ibid.*, **74**, 1297 (1952)).

The hybrid structure is in better agreement with the chemical and physical properties of these compounds.[3] It also accounts for the non-existence of certain structural isomers which are predicted from the "furoxane" representation. For example, 4- and 5-methyl-ψ-1,2-dinitrosobenzene are identical.[3a,b] There is no apparent reason why hydroxy or primary amino derivatives of "benzfuroxane" do not exist[5]; however, recognition of tautomeric forms of hydroxy[5a] and amino dinitrosoaromatic compounds affords an understanding of this fact.

Discussion

Copper or nickel metals in acid solution transformed ψ-*o*-dinitrosoaromatic compounds into *o*-nitroarylamines. Recognition of this unique formation of a nitro compound by a reduction procedure followed the observation of the rapid appearance of color around a nickel spatula in a formic acid solution of ψ-*o*-dinitrosobenzene.

The first reduction product of ψ-*o*-dinitrosobenzene is the dioxime of *o*-benzquinone. Curiously enough this represents the only known method for the preparation of this dioxime.[6] It could not, however, be isolated from the reduction with copper in hydrochloric acid. Experiments with known



(5) (a) T. Zincke and A. Ossenbeck, *Ann.*, **307**, 1 (1899); (b) private communication from R. J. Gaughran, Picatinny Arsenal; (c) unpublished work with U. Toggweiler.

(6) (a) T. Zincke and P. Schwarz, *Ann.*, **307**, 28 (1899); (b) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **101**, 2452 (1912).