was filtered and dried, wt. 10.4 g. (85%), m.p. 115–122°. This product was crystallized from water and identified by melting point and mixture melting point as benzoic acid, m.p. 120.5–122°.

Subsequent repeated extractions of the nonaqueous fraction with dilute hydrochloric acid and basification of the combined extract produced a brown oil which solidified upon cooling. This solid was cambined with the basic product previously obtained, giving a total weight of 5 g., m.p. 71–75°. Crystallization from ligroin (b.p. 65–110°) yielded 4.5 g. (25%) of white crystals, m.p. 73–74.5°. A mixture melting point with authentic *N*-(*o*-hydroxyphenyl)piperidine was undepressed.

The ligroin-insoluble brown residue (0.5 g.) from crystallization was shown by infrared analysis not to be hydroxyphenylpiperidine and was not investigated further.

When the reaction was rerun with a 20:1 molar ratio of phenol to *N*-benzoyloxypiperidine, a 98% yield of benzoic acid and a 32% yield of *N*-(*o*-hydroxyphenyl)piperidine were obtained.

N-(o-Hydroxyphenyl)piperidine. The preparation was adapted from a procedure by Reed.[20] After steam distillation, the product (67% yield) was further purified by crystallization from ligroin (b.p. 65–110°), m.p. 74.2–75°.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.53: H, 8.53; N, 7.90. Found: C, 74.78, H, 8.29; N, 8.10.

N-Benzoyloxypiperidine-toluene.[19] A solution of *N*-benzoyloxypiperidine (38.9 g., 0.19 mole) in toluene (174.8 g., 1.9 moles) was stirred and cooled to 15° in an ice bath. Boron trifluoride was passed into the solution until the gas was no longer absorbed. The reaction mixture, subsequently kept under nitrogen, was heated at 102–107° for 1 hr.

The cooled reaction mixture was extracted repeatedly with dilute ammonium hydroxide. The combined basic extract was extracted with ether which was then added to the organic phase. Acidification of the basic fraction with concentrated hydrochloric acid gave 15.6 g. (67%) of benzoic acid, m.p. 121–123°.

The organic solution was then extracted repeatedly with dilute hydrochloric acid. The combined acid extract was extracted with ether. The acid fraction was made basic with concentrated potassium hydroxide solution producing an oil which was taken up in ether. Removal of the ether from the dried solution left a yellow oil which solidified on standing, wt. 14.2 g. Distillation through an Ace Minilab head gave 7.1 g. of a colorless, viscous oil, b.p. 47–85° (12 mm.) (mostly at 62–63°). The residue in the distillation flask was a dark brown, extremely viscous substance which would not solidify, wt. 5.6 g.

Upon cooling and scratching, the distillate turned to a white crystalline solid, m.p. 62° (damp at 40°), which was crystallized twice from acetone, m.p. 61–70°; lit.[17] α-tripiperideine, m.p. 61–62°; β-tripiperideine, m.p. 72–74°.

Anal.[21] Calcd. for $C_{15}H_{27}N_3$: C, 72.24; H, 10.91; N, 16.85. Found: C, 71.98; H, 10.66; N, 16.74.

Hydrazines and aromatics. General procedure. The mixture of hydrazine compound, aluminum chloride, and toluene (1:2:10 molar ratio) was heated with efficient stirring for 1–2 hr. at 100–110°. The cooled two-phase mixture was poured onto ice and sufficient sodium hydroxide was added to dissolve aluminum hydroxide, followed by standard work-up procedures. No aromatic amine product was obtained in any of the experiments.

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DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CASE INSTITUTE OF TECHNOLOGY
CLEVELAND 6, OHIO

(20) M. C. Reed, U. S. Patent 2,001,584 (1935); *Chem. Abstr.*, 29, 4376 (1935).

(21) By Geller Laboratories, Bardonia, N. Y.

Isolation of 5-Hydroxy-3,6,7,3′,4′-pentamethoxyflavone from *Kuhnia eupatorioides* L. var. *pyramidalis*[1]

WERNER HERZ

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In the course of our studies on sesquiterpene lactones from *Compositae* of this region, we had occasion to investigate *Kuhnia eupatorioides* L. var. *pyramidalis*.[2]

Extraction of the above-ground parts with chloroform followed by the usual work-up[3] gave a gum which was chromatographed over alumina. The only crystalline material which could be isolated was a yellow substance, m.p. 158–159°, which on the basis of its infrared (chelated hydroxyl at 3100–3200, phenyl ketone at 1660 and strong phenyl absorption at 1600 cm.$^{-1}$) and ultraviolet spectrum (λ_{max} 256, 273, and 348 mμ, log ε 4.38, 4.33, and 4.48) appeared to be a hydroxyflavone. The presence of one phenolic hydroxyl and five methoxyl functions suggested by the formula $C_{20}H_{20}O_8$ could be confirmed by conversion to a methyl ether, m.p. 141°, with dimethyl sulfate, and by preparation of an acetate, m.p. 161°. That the free hydroxyl group was in the 5-position of the flavone nucleus was indicated by the infrared spectrum, the color reactions[4] and the resistance to methylation with diazomethane.

The physical and chemical properties of our compound were in good agreement with the properties reported for 5-hydroxy-3,6,7,3′,4′-pentamethoxyflavone (artemetin, artemisetin), a substance synthesized[5] in 1929 and subsequently isolated from *Artemisia arborescens*[6] and *Artemisia absinthium*.[7] A mixed melting point of our material with an authentic sample gave no depression. (m.p. and mixed m.p. reported as 161°.)[8]

The occurrence of quercetagetin derivatives in *Compositae* is thus not limited to members of the tribe *Anthemideae*.

(1) Supported in part by a grant (RG-5814) from the United States Public Health Service.

(2) We are indebted to Professor R. K. Godfrey for collecting and identifying this plant.

(3) W. Herz, R. B. Mitra, K. Rabindran, and W. A. Rohde, *J. Am. Chem. Soc.*, **81**, 1481 (1959).

(4) K. Venkataraman, *Fortschr. Chem. org. Naturstoffe*, L. Zechmeister, ed., Springer Verlag, **17**, 1 (1959).

(5) W. Baker, R. Nodzu, and R. Robinson, *J. Chem. Soc.*, 74 (1929).

(6) Y. Mazur and A. Meisels, *Bull. Research Council Israel*, **A5**, 67 (1955).

(7) Z. Čekan and V. Herout, *Collection Czechoslov. Chem. Communs.*, **21**, 79 (1956).

(8) I wish to thank Dr. V. Herout for carrying out the mixed melting point determination.

EXPERIMENTAL[9]

Finely ground *Kuhnia eupatorioides* L. var. *pyramidalis*, collected near Tallahassee in summer 1958, wt. 3.2 kg., was extracted with chloroform in a Soxhlet extractor for 2 days. The solvent was removed. The residue was taken up in 800 ml. of hot ethanol and diluted with 900 ml. of hot water containing 25 g. of lead acetate and 5 ml. of acetic acid. After 1 day the mixture was filtered, the brown filtrate was concentrated at reduced pressure and then extracted thoroughly with chloroform. Drying followed by removal of chloroform yielded 31 g. of viscous gum which could not be induced to crystallize.

The major part, 25 g., was taken up in benzene and chromatographed over 300 g. of alumina (Alcoa Grade F-20). Fractions 1–7 (150 ml. each of benzene) eluted a trace of oil, fractions 8–23 (150 ml. each of chloroform) eluted gum containing crystalline material as did fraction 24 (1.5 l. of 9:1 chloroform-methanol). On trituration with a small amount of ether, the gum dissolved, leaving a total of 1.1 g. of crystalline material from fractions 8–24. Repeated recrystallization from acetone-ether yielded 0.42 g. of yellow needles of artemetin, m.p. 158–159°, lit.159°,[5] 161.5,[7] 163–164°,[6] olive-green color with alcoholic ferric chloride solution, intense yellow color with alcoholic potassium hydroxide and cond. sulfuric acid, salmon-pink color on treatment with magnesium and hydrochloric acid.

Anal. Calcd. for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19; $-OCH_3$, 38.37. Found: C, 61.86; H, 5.25, $-OCH_3$, 38.03.

A solution of 0.07 g. of the flavone in 1 ml. of pyridine was treated with 0.5 ml. of acetic anhydride, warmed on the steam bath for one hour and allowed to stand overnight. Dilution with water followed by two recrystallizations from methanol–methylene chloride yielded colorless fluffy needles of 5-acetoxy-3,6,7,3′,4′-pentamethoxyflavone, m.p. 160.5–161.5°, lit.[6] 162–163°. The procedure recommended by Mazur and Meisels[6] gave impure material.

Anal. Calcd. for $C_{22}H_{22}O_9$: C, 61.39; H, 5.15. Found: C, 61.24; H, 5.08.

A solution of 0.14 g. of the flavone in 15 ml. of acetone was treated with 0.5 ml. of dimethyl sulfate and 5 ml. of 15% potassium hydroxide solution and allowed to stand for 12 hr. with occasional shaking. Dilution with water followed recrystallizations from acetone-water gave long needles, faintly tinged with yellow, of quercetagetin hexamethyl ether, m.p. 140.5–141.5°, lit. m.p. 141°,[6] m.p.[6,7] 142–143°.

Anal. Calcd. for $C_{21}H_{22}O_8$: C, 62.68; C, 72.68; H, 5.51. Found: 65.59; H, 5.59.

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THE FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLA.

(9) Melting points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford, England. Ultraviolet spectra were determined on a Cary recording spectrophotometer in 95% ethanol solution.

Optical Rotatory Dispersion Studies on Polysaccharides. III. Amylose, Amylopectin, and Methylcellulose[1]

W. BROCK NEELY

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This paper is a continuation of the work in this laboratory on the conformation of polysaccharides in solution.[2,3] Solutions of amylose, amylopectin, and partially methylated cellulose were examined using the technique of optical rotatory dispersion. The method was similar to that used on protein and polypeptide solutions.[4] Typical plots of the dispersion data are shown in Fig. 1, and the values for λ_c and $[\alpha]_D$ are given in Table I for the various polysaccharide solutions.

TABLE I

ROTATORY DISPERSION CONSTANTS OF POLYSACCHARIDE SOLUTIONS

Polysaccharide	Solvent	λ_c, (mμ)	$[\alpha]_D$
Amylose (0.4 g./100 ml.)	Water	135	+200
	0.5*M* KCl	134	+201
	8*M* urea	132	+200
	1*M* NaOH	132	+162
	DMSO[a]	210	+175
Amylopectin (0.4 g./100 ml.)	Water	135	+200
	1*M* NaOH	134	+163
Methylcellulose (2 g./100 ml.)	Water	Anomalous dispersion	
solubilized at room temp.[b]	8M urea	235	−7.44

[a] DMSO = dimethylsulfoxide, see ref. 6 for details of dispersing amylose in this particular solvent. [b] See Ref. 3 for details of solubilization.

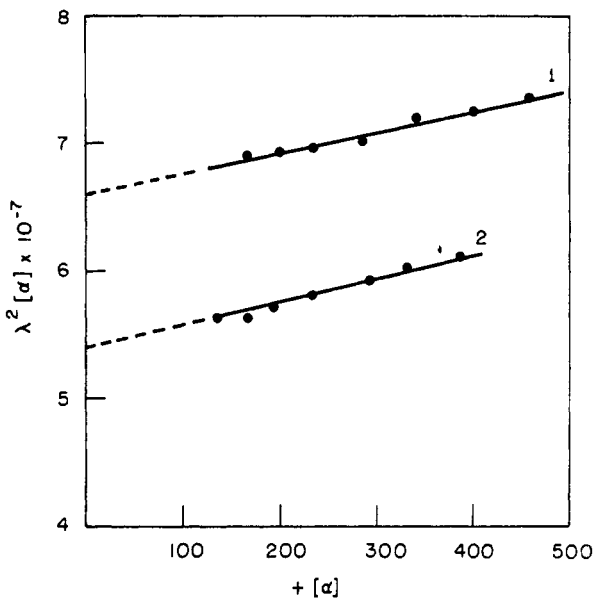

Fig. 1. Modified Drude plots of rotatory dispersion data on amylose solutions. Curve 1, amylose (0.4 g./100 ml.) in water; curve 2, amylose (0.4 g./100 ml.) in 1*M* sodium hydroxide

The value of λ_c for amylose and amylopectin in aqueous and 1*M* sodium hydroxide solutions was constant. This independence of λ_c demonstrates that rotatory dispersion is unable to measure any

(1) Presented in part at the 138th American Chemical Society Meeting, New York, N. Y., September, 1960.
(2) W. B. Neely, *Nature*, **185**, 159 (1960).
(3) W. B. Neely, *J. Am. Chem. Soc.*, **82**, 4354 (1960).
(4) E. R. Blout, *Optical Rotatory Dispersion: Applications to Organic Chemistry*, C. Djerassi ed., McGraw-Hill, New York, 1960, chap. 17.