The 2,4-Dinitrophenylhydrazones of Some Flavanones[1,2]

BY CARL D. DOUGLASS, QUENTIN L. MORRIS AND SIMON H. WENDER

In an attempt to prepare new derivatives to aid in the identification of naturally occurring flavonoid compounds, the 2,4-dinitrophenylhydrazones of eight flavanones have been prepared. This derivative of the two compounds flavanone and flavone has previously been reported by Mozingo and Adkins.[3] The preparation of the 2,4-dinitrophenylhydrazones of several flavonols (aglycones and glycosides) has also been attempted by several procedures during this investigation, but has thus far been unsuccessful.

When the flavanone derivatives are freshly prepared, they yield very distinctive crystals which may be of value in the identification with a microscope of the parent compounds.

Experimental

The stock solution of the 2,4-dinitrophenylhydrazine was prepared by adding 1 g. of 2,4-dinitrophenylhydrazine to 2 ml. of concentrated sulfuric acid. Sufficient undenatured 95% ethanol, about 60 ml. usually, was used to dissolve all the solid present. This was made up fresh and used while hot.

To 2 ml. of this resulting solution in a test-tube, 20 mg. of the flavanone was added. After solution had been effected by agitation, the tubes were heated to boiling in a water-bath and then allowed to cool slowly. The derivatives separated on standing.

TABLE I

2,4-Dinitrophenylhydrazone of	M.p., °C.	R_f	Nitrogen, % Calcd.	Found
Butin	249–247	0.80	12.39	12.29
4′,7-Dihydroxy-3′,5′-dimethoxyflavanone	250	0.87	11.32	10.41
4′,7-Dihydroxy-3′-methoxyflavanone	255 dec.	0	12.01	12.36
Hesperitin	293 dec.	0.81	11.61	11.13
Homoeriodictyol	295 dec.	0	11.61	11.29
7-Hydroxyflavanone	272	0	13.33	13.16
Liquiritigenin	258–259	0	12.83	12.90
Naringin	246–247	0.98	7.37	6.82

After filtration through sintered glass, the compounds were recrystallized by dissolving in a minimal quantity of boiling dioxane and adding water dropwise to incipient cloudiness. The solutions were then allowed to stand in the cold for several hours and filtered. The solids were washed with cold ethanol and ether and dried at 100° for 2 hours. Yields of between 40 and 60% were obtained.

The derivatives are sparingly soluble in ethanol, ether and acetone, but very soluble in dioxane. While in the solid state, the compounds are red, but in acetone or dioxane they yield yellow solutions. They also act as acid–base indicators, exhibiting a yellow color in acid and a dark violet in base.

The absorption spectra of the dinitrophenylhydrazones of hesperitin, liquiritigenin and 7-hydroxyflavanone were determined in 95% ethanol by using the Beckman model DU spectrophotometer in the range of from 220 to 500 mμ. The spectra are quite similar. The only major absorption band occurs at approximately 400 mμ.

The compounds were subjected to one-dimensional paper chromatography using the method of Wender and Gage[4] in a solvent mixture consisting of 50% water, 30% dioxane and 20% glacial acetic acid (by volume). The R_f values are given in Table I.

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(2) Presented before the Sixth Southwest Regional Meeting of the American Chemical Society, December 7–9, 1950, San Antonio, Texas.

(3) R. Mozingo and H. Adkins, THIS JOURNAL, **60**, 669 (1938).

(4) S. H. Wender and T. B. Gage, *Science*, **109**, 287 (1949).

Infrared Spectra of Rotenone and Dihydrorotenone

BY H. L. CUPPLES AND I. HORNSTEIN

The chemical structures of rotenone and its derivatives were determined almost simultaneously by LaForge and Haller,[1] Butenandt and McCartney,[2] and Takei, Miyajima and Ono.[3] The present paper is concerned with the determination and interpretation of the infrared spectra of rotenone and dihydrorotenone. A comparison of the chemical structures and infrared spectra of these compounds has proven to be of considerable interest.

Experimental

The rotenone was obtained by exhaustive chloroform extraction of ground and dried *Tephrosia virginiana* roots. The solvent was removed under vacuum. To the viscous sirup an excess of ether was added; on standing a precipitate of rotenone formed. The crude rotenone precipitate was recrystallized twice from carbon tetrachloride, and the rotenone–carbon tetrachloride solvate was in turn twice recrystallized from ethanol. The purified product had a melting point of 163° in Pyrex and when mixed with an authentic sample of rotenone showed no melting point lowering; $[\alpha]^{20}D$ was −230° in benzene.

Dihydrorotenone was prepared by hydrogenating rotenone with a Raney nickel catalyst.[4] Five grams of rotenone in 100 ml. of ethyl acetate was shaken in a hydrogen atmosphere with 1.5 g. of the nickel catalyst until 280 ml. of hydrogen was absorbed. The solution was filtered and the solvent removed under vacuum. The residue was dissolved in chloroform and the solution was extracted with 5% potassium hydroxide. The chloroform was removed from the alkali-insoluble major fraction and the residue recrystallized twice from a benzene–ethanol mixture. The yield was 4 g. and the product melted at 216° in Pyrex. When it was mixed with an authentic sample of dihydrorotenone, no melting point depression was noted; $[\alpha]^{20}D$ was −225° in benzene.

The solubilities of rotenone and dihydrorotenone in carbon tetrachloride were found to be 7.7 and 8.9 g./l., respectively; in carbon bisulfide the solubilities were found to be >20 and 9.9 g./l., respectively. Between 2.0 and 7.5 microns both spectra were determined in carbon tetrachloride solution, at a concentration of 7.0 g./l. Between 7.5 and 15.0 microns the solvent was carbon bisulfide, rotenone at 20.0 g./l. and dihydrorotenone at 9.9 g./l.

Infrared spectra were obtained on a commercial single-beam, recording, rock-salt prism spectrometer, and corrections for solvent absorption were made by calculating and replotting on a point to point basis.[5] Percentage transmissions for each compound over the 2 to 15 micron range are presented in Fig. 1.

Discussion

In the hydrogenation of rotenone to dihydrorotenone the double bond of the isopropenyl side chain

(1) F. B. LaForge and H. L. Haller, *ibid.*, **54**, 810 (1932).

(2) A. Butenandt and W. McCartney, *Ann.*, **494**, 17 (1932).

(3) S. Takei, S. Miyajima and M. Ono *Ber.*, **65**, 1041 (1932).

(4) H. L. Haller and P. S. Schaffer, (a) *ibid.*, **55**, 3494 (1933); (b) *Ind. Eng. Chem.*, **25**, 983 (1933); (c) U. S. Patent 1,945,312.

(5) H. L. Cupples, THIS JOURNAL, **72**, 4522 (1950).

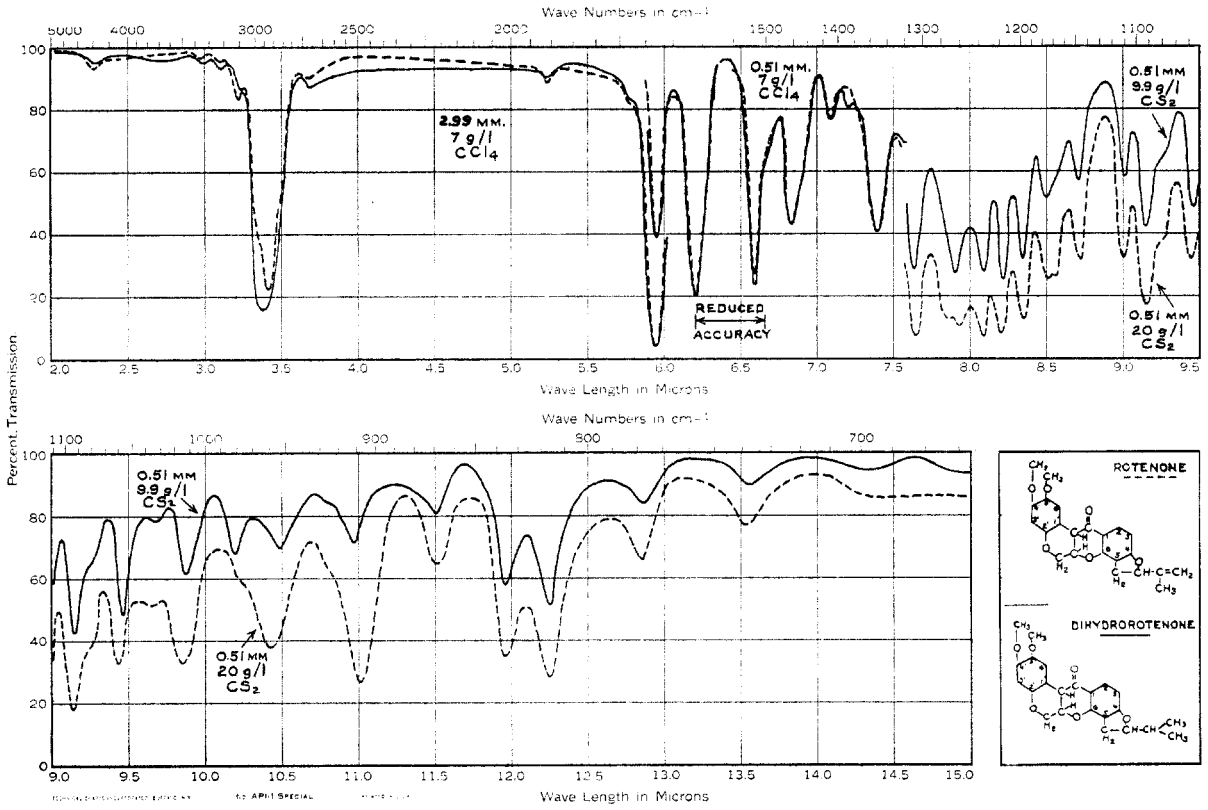

Fig. 1.

is saturated and there is formed the corresponding isopropyl grouping. It is of interest to see whether evidences of this chemical change can be observed in the infrared spectra.

In the 3.4-micron region (C–H vibrations) the hydrogenation results in a filling-in and general strengthening of the absorption envelope. The rock-salt prism resolution does not suffice to resolve any of the individual bands of the dihydrorotenone spectrum in this region, but the spectrum of rotenone does show a minimum at about 3.23 microns which is probably associated with the terminal methylene group.[6,7] An overtone which is shown by Colthup in the vicinity of 5.63 microns is not observed for rotenone, and there are no observed differences in the spectra in the 5.4–6.8 micron (double-bond) range, but differences in the latter region may well be obscured by overlapping C=O absorption or by the lessened accuracy caused by strong solvent absorption. Dihydrorotenone alone has a weak minimum at 7.21 microns which may be associated with the isopropyl group. The greatest differences in absorptivity appear in the 9.5 to 11.0 micron range. Rotenone has relatively strong absorption at about 11.0 microns, which falls within the range given by Colthup for a strong characteristic absorption of the vinyl group. Dihydrorotenone has relatively strong absorption at about 10.2 microns, at the short wave length end of the range given by Colthup for a weak characteristic absorption of the isopropyl group.

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(6) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

(7) E. L. Saier and N. D. Coggeshall, *Anal. Chem.*, **20**, 812 (1948).

The Hammett Acidity Function in 6 Formal Perchloric Acid–Sodium Perchlorate Mixtures

BY GARMAN HARBOTTLE[1]

Hammett[2] has defined an acidity function H_0 by the equation

$$H_0 = -\log (a_{H^+} f_B / f_{BH^+})$$

in which a_{H^+} is the activity of hydrogen ion and f_B and f_{BH^+} are the activity coefficients of a neutral base B and its conjugate acid BH^+, respectively. The quantity H_0 may be estimated, for a particular solution, by colorimetric measurements of the degree of conversion of certain indicator bases to their conjugate acids. The technique has been described by Hammett and Deyrup.[3]

The acidities H_0 of aqueous solutions of several acids have been reported in detail by Hammett and Paul[4] and Hammett and Deyrup.[3] In this note values of the acidity function in mixed perchloric acid–sodium perchlorate solutions of constant ionic strength 6.0 formal (moles solute per liter solution) are reported.

Experimental

Three indicators were used in these measurements. The compounds, and the logarithmic acidity constants of their conjugate acids, as reported by Hammett[2] were *o*-nitroaniline (pK_a −0.19), *p*-chloronitroaniline (pK_a −0.91) and 2,4-dichloro-6-nitroaniline (pK_a −3.18). The first two indicators were purchased from Eastman Kodak Co. while the third was prepared from the second by chlorination accord-

(1) Brookhaven National Laboratory, Upton, New York.

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 266–267.

(3) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

(4) L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).