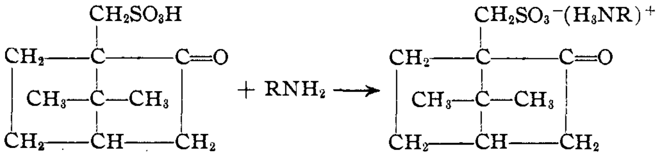
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# Anomalous Mutarotation of Salts of Reychler's Acid. V. Comparison of the Absorption Spectrum of 2-(N-Methylimino)-*d*-camphane-10-sulfonic Acid with the Spectra of other Camphane Derivatives

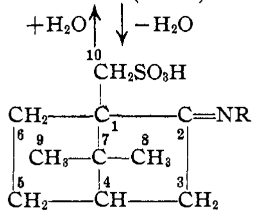
BY R. L. SHRINER AND HARRY SUTHERLAND

Primary amine salts (II) of Reychler's acid (I) have been shown to undergo dehydration[1] to produce a compound whose chemical properties are in agreement with the ketimine structure shown by formula (III). The optical properties, however, are still somewhat puzzling since Reychler's acid and its salts are *dextro*-rotatory whereas the ketimines are strongly *levo*. It is difficult to understand why the relatively simple structural change from the $-\underset{|}{C}=O$ to $-\underset{|}{C}=N-$ in the 2-position should cause a reversal in optical rotation when there is no change in the configuration about the asymmetric carbon atoms 1 and 4. Since the compounds are colorless the difference must be associated with the ultraviolet absorption. If Reychler's acid and the ketimine possessed markedly different absorption spectra, the reversal in rotation would be understandable since it is known that the direction of rotation of an optically active compound is related to its absorption spectrum.[2] Hence a study was made of the absorption spectra of Reychler's acid (I), 2-oximino-*d*-camphane-10-sulfonic acid (V) and 2-(N-methylimino)-*d*-camphane-10-sulfonic acid (VI).

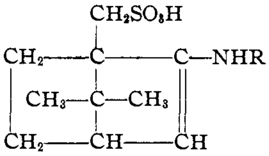


I
Reychler's acid (*dextro*)

II
Amine salt (*dextro*)



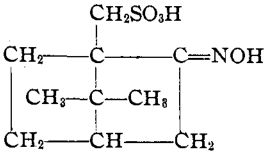
III
Ketimine (*levo*)



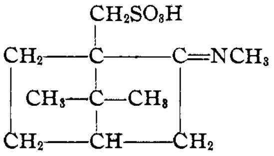
IV
Ene-amine

There is also a possibility that the ketimine could tautomerize to an ene-amine[3] structure, such as shown in formula IV, although the chemical evidence[1] is against such a structure. In order to exclude such a change it was desirable to compare the absorption spectrum of the ketimine with that of bornylene which is known to have a double bond between carbon atoms 2 and 3.

The absorption spectra of these compounds were determined in 95% alcohol since solutions of suitable concentration of all the compounds could be prepared in this solvent. The data obtained are summarized in the curves shown in Fig. 1. The curve for camphor is also included although its absorption spectrum has been determined by several investigators[4] in other solvents.



V



VI

An inspection of the curves in Fig. 1 shows several interesting points.

1. The curves for camphor (A) and Reychler's acid (B) which are both dextrorotatory are quite similar. The introduction of the sulfonic acid group in the 10-position of camphor has modified the curve only slightly in the region of 2300 to 2450 Å. and 3025 to 3150 Å. The curve for camphor is very similar to that previously reported by Kuhn and Gore.[4] The position of maximum absorption has shifted due to the change in solvents from hexane to 95% alcohol. Part of the absorption curve for Reychler's acid had also been determined previously.[5] The results are in agreement with those obtained in the present work.

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[1] Schreiber and Shriner, THIS JOURNAL, **57**, 1306, 1445, 1896 (1935); Sutherland and Shriner, *ibid.*, **58**, 62 (1936).

[2] Lowry, "Optical Rotatory Power," Longmans, Green and Co., London, 1935, Chap. XXIV.

[3] (a) See Baker, "Tautomerism," George Routledge and Sons, London, 1934, pp. 122 ff.; (b) Stevenson and Johnson, THIS JOURNAL, **59**, 2525 (1937).

[4] Kuhn and Gore, *Z. physik. Chem.*, **12B**, 389 (1931); ref. 2.

[5] Lowry and Owen, *J. Chem. Soc.*, 606 (1926).

2. The curves for the oxime (C) and the ketimine (D) both of which are levorotatory are similar to each other and are markedly different from that of Reychler's acid from which they are derived. The absorption exhibited by these two levorotatory compounds is much more intense and at an entirely different position. In fact the maxima in the absorption curves for these two compounds are shifted so far into the ultraviolet region that the complete curve could not be obtained. It is evident that the introduction of the $>C{=}N-$ grouping in place of the $>C{=}O$ group in the 2-position has caused a profound change in the absorption of light by the molecule.

The results parallel a previous study of camphor-10-sulfonanhydramide by Lowry[6] who pointed out that this compound differs from Reychler's acid in that it was levorotatory and did not show the ketonic absorption band in the vicinity of 3000 Å.

3. Bornylene and camphane showed no absorption in 95% alcohol in the range studied. The fact that bornylene, which has a double bond between carbon atoms 2 and 3, showed no absorption, whereas the ketimine did, indicates that no tautomerization to the ene-amine structure (IV) occurred. The similarity of the ketimine curve (D) to that for the oxime (C) is also evidence against the ene-amine structure (IV) and in favor of the ketimine structure (III).

## Experimental

**Camphor.**—The naturally occurring dextrorotatory camphor was resublimed. It melted at 176–177° and had a specific rotation of +44.0° in chloroform (*c*, 2.0).

**Reychler's Acid (*d*-Camphor-10-sulfonic Acid.)**—Sulfonation of camphor by a modification[7] of Reychler's original method gave a 45% yield. The monohydrated form of the acid was used. Its neutral equivalent was 250.0 (calcd. 250.2) and its specific rotation[8] was +42.0° in absolute ethanol (*c*, 3.0).

**2-Oximino-*d*-camphane-10-sulfonic Acid.**—Treatment of *d*-camphor-10-sulfonic acid with hydroxylamine according to the directions of Reychler[9] gave the oxime which was recrystallized twice from 95% ethanol. It melted at 176.5–177.5° and had a specific rotation of −123.6° in methanol (*c*, 1.0).

**2-(N-Methylimino)-*d*-camphane-10-sulfonic Acid.**—One sample of this ketimine was prepared according to the method previously described[1] except that the methylamine salt of Reychler's acid was heated to 184° *in vacuo* instead of at atmospheric pressure. Four recrystallizations from absolute alcohol with the use of Norite were necessary in order to obtain a pure product.

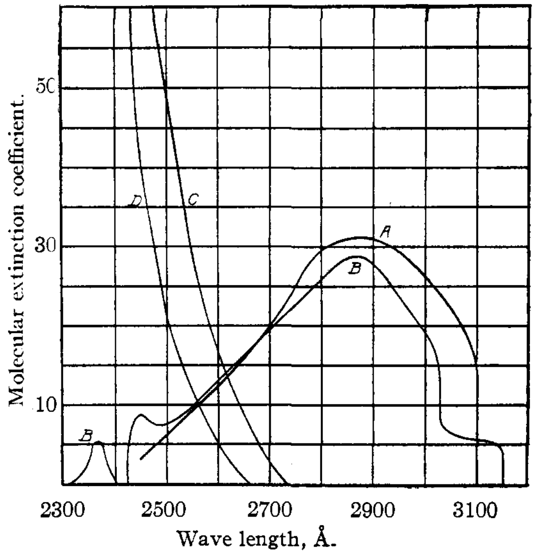

Fig. 1.—Camphor = A; Reychler's acid = B; 2-oximino-*d*-camphane-10-sulfonic acid = C; 2-(N-methylimino)-*d*-camphane-10-sulfonic acid = D.

A modified procedure was developed which yielded a product more easily purified. To a solution of 6.8 g. of methylamine in 100 cc. of ethanol were added 30 g. of *d*-camphor-10-sulfonic acid and 150 g. of ethylene glycol. The mixture was distilled until the volume of the residue was about 50 cc. This residual solution was cooled and the ketimine filtered and washed with cold alcohol. Recrystallization from absolute alcohol gave 12.8 g. of colorless crystals which melted at 312–313° (Maquenne block) and possessed a specific rotation of −137.6° in ethanol (*c*, 1.0).

***l*-Bornylene.**—The preparation of pure *l*-bornylene is extremely difficult owing to the fact that the product invariably is contaminated with tricyclene or *d*-camphene which cannot be separated readily from *l*-bornylene. The pyrolysis of methyl bornyl xanthate as described by Chugaev and Budrick[10] gave a product which contained 25% of tricyclene even after it had been subjected to the purification process recommended by Henderson and Caw.[11]

The Hofmann exhaustive methylation of bornylamine and subsequent pyrolysis of the quaternary ammonium hydroxide gave a sample of *l*-bornylene which melted at 109° and had a specific rotation of −18.1° in methanol (*c*, 2). The highest recorded rotation is −22.3° obtained by Henderson and Caw.[11] The sample of bornylene obtained was only about 96% pure, the chief impurity being *d*-camphene. Since no absorption was shown by this sample of *l*-bornylene in the range 2300 to 3500 Å., no further attempts to obtain absolutely pure *l*-bornylene were made.

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(6) Lowry and Desch, *J. Chem. Soc.*, **95**, 1340 (1909); Richards and Lowry, *ibid.*, **127**, 1503 (1925).

(7) Adams, Kamm and Marvel, "Organic Chemical Reagents," *Univ. of Ill. Bull.*, **18**, No. 6 (1920).

(8) All specific rotations were made at 25° with sodium D light: concentration, *c*, in g. per 100 cc. of solution.

(9) Reychler, *Bull. soc. chim.*, [III] **19**, 120 (1898).

(10) Chugaev and Budrick, *Ann.*, **388**, 280 (1912).

(11) Henderson and Caw, *J. Chem. Soc.*, **101**, 1416 (1912).

**Absorption Measurements.**—The Bausch and Lomb Littrow-type spectrograph was used with a sectorphotometer. This instrument gave simultaneous adjacent records on the photographic plate of light transmitted by solvent and solution in identical cells. The ratio of the exposures was governed by the setting of the sector wheels. Solutions of the compounds were made up to a concentration of 0.005 molar in 95% aldehyde-free ethanol.[12] This concentration was chosen because it gave reasonable absorption for camphor. The cells were 50 mm. in length. The source of illumination was an iron arc operating at about 25 amperes and all wave lengths were obtained from the iron lines themselves.

Positions of equal intensity in the adjacent spectra, transmitted by solvent and solution, were read visually on the negatives with the aid of a microprojector and a mask which obscured all but corresponding portions 1 mm. wide in the spectra, in order to prevent variations in the intensities of the lines from top to bottom from affecting the readings. The molecular extinction coefficient is defined by the equation[2] (p. 378)

$$I = I_0 10^{-\epsilon c l}$$

which may be written in the form

$$\epsilon = \frac{1}{cl} \log_{10} \frac{I_0}{I}$$

Since $\log_{10} I_0/I$ = sector setting of the instrument

$$\epsilon = \text{sector setting}/cl$$

$c$ being concentration in moles per liter and $l$ length of cell in centimeters.

The extinction coefficients were plotted against wave length and the data obtained have been summarized in Fig. 1.

**Acknowledgment.**—The authors wish to express their appreciation to the University of Wisconsin for the use of the spectrograph. They are especially indebted to Dr. V. W. Meloche for his kindness and helpful suggestions during the making of the ultraviolet absorption measurements.

### Summary

The ultraviolet absorption spectrum of the compound obtained by the dehydration of the methylamine salt of Reychler's acid, and that of the oxime of this acid (both of which are levorotatory) are quite similar to each other but differ markedly from the absorption spectra of *d*-camphor and Reychler's acid (both of which are dextrorotatory). These absorption data, together with the fact that bornylene showed no absorption in the same range of wave length studied, indicate that no ene-amine structure is present and that the levorotatory dehydration product is 2-(N-methylimino)-*d*-camphane-10-sulfonic acid.

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[12] Stout and Schuette, *Ind. Eng. Chem., Anal. Ed.*, **5**, 100 (1933).

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[CONTRIBUTION FROM THE U. S. REGIONAL SOYBEAN INDUSTRIAL PRODUCTS LABORATORY[1]]

# Peptization of Soybean Proteins. The Effect of Neutral Salts on the Quantity of Nitrogenous Constituents Extracted from Oil-Free Meal

BY ALLAN K. SMITH, SIDNEY J. CIRCLE AND GEORGE H. BROTHER

## Introduction

A review of the literature discloses that no systematic study on the salt peptization of soybean proteins has been made. Most workers[2–4] in this field have followed to a great extent the lines laid down by Osborne and Campbell,[5] who identified the principal protein in soybeans as a globulin which they called glycinin. They also found a second globulin which resembled phaseolin, about 1.5% of albumin and a small amount of proteose.

Recently Ryndin[4] studied the physical chemistry of soybean proteins. This work involved the preparation of glycinin according to Osborne's procedure, and includes data on the extraction of protein from soybean oil-free meal by sodium chloride solutions of several concentrations. He shows variation in the amount of nitrogenous matter extracted, but no general conclusions concerning salt peptization of soybean meal may be drawn, as he has studied the effect of only one salt.

In recent years it has been shown that the amount of protein extracted from seeds by neutral salts depends upon the kind and concentration of the salt used.[6–8] It was therefore decided that

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[1] A coöperative organization participated in by the Bureaus of Chemistry and Soils and Plant Industry of the U. S. Department of Agriculture, and the Agricultural Experiment Stations of the North Central States of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.

[2] Jones and Csonka, *Am. Soc. Biol. Chem. Proc.*, **26**, XXIX (1932).

[3] Hartman and Cheng, *J. Chinese Chem. Soc.*, **4**, 152 (1936).

[4] Ryndin, *Colloid J.* (*U. S. S. R.*), **2**, 811 (1936).

[5] Osborne and Campbell, THIS JOURNAL, **20**, 419 (1898).

[6] Gortner, Hoffman, and Sinclair, *Colloid Symposium Monograph*, **5**, 179 (1928).

[7] Staker and Gortner, *J. Phys. Chem.*, **35**, 1565 (1931).

[8] O'Hara and Saunders, THIS JOURNAL, **59**, 352 (1937).