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ULTRAVIOLET ABSORPTION OF A SERIES OF EIGHT ORGANIC SUBSTANCES OF THE GAMMA-PYRIDONE TYPE, IN WATER SOLUTION[1]

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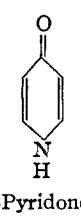
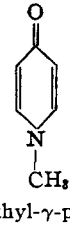
γ-Pyridone, N-methyl-γ-pyridone, and γ-pyrone are probably the simplest heterocyclic substances possessing the considerable unsaturation which is briefly designated by the term quinonoid; these three substances, which constitute Group A in the series of compounds studied, should have selective absorption in the ultraviolet. The three substances may also be obtained with two carboxyl groups in the molecule, similarly placed, so that the resulting acids are as closely related to each other as are the members of Group A. The acids form Group B in the series; as they still have the quinonoid structure, they too should show selective absorption in the ultraviolet. Finally, the unsaturation may be removed in the two pyridones,[2] but leaving the ring structure; the reduced substances form Group C. It seemed worth while to find the absorption bands, determine their position when found, and particularly their persistence. Not only may the three groups be compared in order to find the effect of weighting the molecule and of removing the unsaturation, but in each group the members may be compared to one another in order to determine the effect of replacing NH by NCH_3 or by O. The eight substances thus form an interesting series; and as it was found possible to use water as solvent in each case, any complication on the score of solvent is avoided.

The series is as follows:

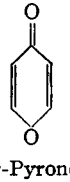
Group A



γ-Pyridone



N-Methyl-γ-pyridone

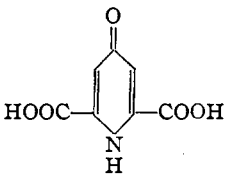


γ-Pyrone

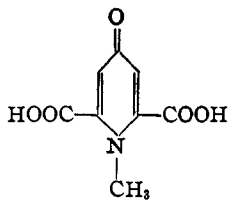
[1] Presented before the Organic Division at the Los Angeles Meeting, August, 1925.

[2] To reduce pyrone without opening the ring has not been accomplished, to our knowledge; tetrahydro-pyrone has been made [Borsche, *Ber.*, **48**, 682 (1915)] and we repeated the preparation and examined the body for its ultraviolet absorption but, in spite of considerable work, we do not feel certain enough of its purity to include it; we are the more inclined to omit it because it still has the ketone group, and is, therefore, not strictly comparable to γ-hydroxy-piperidine and its N homolog.

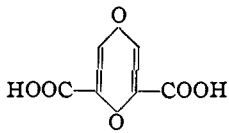
Group B



Chelidamic acid

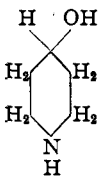


N-Methyl-chelidamic acid

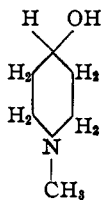


Chelidonic acid

Group C



γ-Hydroxy-piperidine



N-Methyl-γ-hydroxy-piperidine

Previous Investigations

As far as our search has revealed, none of these substances has been studied in pure water solution. N-Methyl-γ-pyridone, chelidamic acid, N-methyl-chelidamic acid, γ-hydroxy-piperidine, and N-methyl-γ-hydroxy-piperidine, have never been studied as to their absorption in the ultraviolet, in any solvent. The remaining three substances have been examined before but for other purposes and under conditions which preclude any agreement with the present results. γ-Pyrone has been observed in alcohol solution, with and without sodium ethoxide;[3] in alcohol it was found to have no band; in alcohol with one equivalent of sodium ethoxide, it has a band at about 3200 Å., whereas we found it to have, in pure water solution, a band at 2450 Å. Chelidonic acid has been studied in water containing 100 equivalents of sodium hydroxide[4] when it showed two bands, at about 4000 Å. and 2800 Å.; we found chelidonic acid in pure water solution to have only one band, at 2700 Å. γ-Pyridone was studied, in alcoholic solution probably,[5] in alcohol containing hydrogen chloride, and in alcohol containing sodium ethoxide; none of the results are similar to those reported herein.

Procedure

The instrument in which the solutions were tested for their absorption in the ultraviolet was a Hilger quartz spectroscope, size C, with a Hilger sector photometer; the latter has two rotating sectors, one of which, the upper, is adjustable and controls the comparison spectrum. The

[3] Baly, Collie and Watson, *J. Chem. Soc.*, **95**, 144 (1909).

[4] Ref. 3, p. 154.

[5] Baker and Baly, *J. Chem. Soc.*, **93**, 1128 (1907); that alcohol was the solvent must be inferred from the article; it is not clearly stated.

source of light is an under-water spark[6] which gives a continuous spectrum in the ultraviolet practically free from lines. The path of the light lies only through water, air and quartz. The range of the wave lengths is from 7000 Å. to 2100 Å.; the width of the slit was 0.1 mm. The plates are approximately 25 by 10 cm., and can record as many as 15 exposures; each absorption spectrum has contiguous to it a comparison spectrum by means of which the points of equal blackening are found; a wave-length scale is photographed at the top and at the bottom of the plate; its correct placement is determined with the help of the lines from copper.

The adjustable sector is graduated in divisions that represent the logarithms of the ratio of fractions of whole revolutions performed by the two sectors, and this ratio is inversely proportional to the ratio of the light which passes through the two sectors.

For each wave length, $\log t_1/t_0 = k \log I_0/I_{tr}$, in which t_1 equals the fraction of whole revolutions of the adjustable sector, t_0 the fraction of whole revolutions of the fixed sector, I_0 is the light entering the absorption cell, and I_{tr} is the light transmitted, equal, at the place of equivalent blackening, to the light passing through the adjustable sector; k may be set equal to one. For each sector opening the period of the exposure is of predetermined duration.[7]

The light for the comparison spectrum does not pass through a cell, but is sent through the adjustable sector to one face of the bi-prism covering the slit. The fixed sector is fitted with a cell, with quartz windows, which is filled with the solution to be tested; that the solvent used, water, was indeed optically void, was established at regular intervals. The cells used were of various thicknesses, 1 cm., 0.5 cm. and 0.1 cm.

Once the proper dilution has been determined by preliminary tests, the cell is filled and no further change is necessary; instead of further dilution, or change in the thickness of the cell, the period of illumination is varied; the short exposure corresponds to low dilution, the long exposure to high dilution. The exposures which have a value lie between two limits: the shortest exposure must cause on the plate no measurable blackening, the longest exposure must show almost continuous blackening and, hence, must no longer show one or more bands; the exposures showing the location of the band lie between these two limits.[8]

[6] Set up as described in *Sci. Papers Bur. Standards*, No. 440, vol. **18** (1922), except that the two rotating zinc disks for the outside spark are replaced by two adjustable horizontal zinc rods, with a blast of air directed into the gap.

[7] A table showing the exposures corresponding to the sector openings is furnished with the instrument; the period is the number, expressed in our case in minutes, of which the sector opening is the logarithm, multiplied by a constant whose value depends upon the arrangements; in our case, it was 1.

[8] We have assumed that Beer's law holds: no determination with one of the substances included in the series has been made other than casual observations in the course

The points at which the blackening in the absorption spectrum is equal to the blackening of the contiguous comparison spectrum are determined, in the dark room, by placing the plate on a ground glass illuminated from beneath; the approximate location is noted, then all but a small area surrounding the point is covered by a sheet of black paper fitted with an elliptical hole; with the aid of a lens mounted on a small tripod, the area is studied and the exact point marked with a fine pen. The paper is removed and the wave length corresponding to the point determined by means of the scale photographed at the top and bottom of the plate. The smallest division on the scale is 10 Å.; fractions of this amount are estimated.

The molecular extinction coefficient is computed by the formula $\epsilon = (1/d) \times (1/C) \times (\log I_0 - \log I_{tr})$, wherein d is the thickness of the cell in centimeters, C is the concentration in terms of molal solution, and $(\log I_0 - \log I_{tr})$ is the logarithm of the sector opening. For each plate, a factor containing $1/d$ times $1/C$ was computed so that the plate formula was simplified to ϵ = plate constant $\times$ sector opening. For example, with γ-pyridone, Group A, Table I, the plate constant is $[1/(^1/_2)] \times [1/(^1/_{8358})] = 167.1 \times 100$; hence, for the sector opening 0.2, the molecular extinction coefficient is $\epsilon = 0.2 \times 167.1 \times 100 = 33.4(2) \times 100$.

For the sector opening marked 0, the time of exposure is one minute, the shortest exposure; for the sector opening marked 1.3, the time is 19 minutes and 57 seconds, the longest exposure in this investigation.

In preparing the graphs, a provisional curve is first plotted in which the sector openings are the ordinates, the wave lengths, the abscissas; the molecular extinction coefficients are calculated and entered for each sector opening; as they are uneven numbers for the various openings, the points on the curve corresponding to even multiples of one hundred are marked off, and from these the final curve is plotted. It is for this reason that circles showing experimental points do not appear on the curves. The readings from the plates in wave lengths with the corresponding sector openings are given in tabular form; the readings are made from the red end as starting point.

All solutions were at room temperature.

In order to indicate the degree of accuracy of the values obtained, the various possible sources of error were either determined experimentally or estimated from theoretical considerations.

The limit of the sensitiveness of the plate to a change in light was found to be such that a difference in sector opening of 0.025 gave blackenings that could just be distinguished. We have, therefore, assumed that the opening

of preliminary tests; these indicated that the law holds. We did make a special test on this point with tyrosine, a substance similar to the present ones. The curves for absorption with a 5cm. tube and dilution 0.0002 *M*, 1cm. tube and dilution 0.001 *M*, 0.2cm. tube and dilution 0.05 *M*, were plotted on one paper and found to agree within the usual error of reading.

0.020 would no longer give blackenings that could be distinguished. The error may be in either direction.

A certain amount of reflection of light by the absorption cell takes place, which has no counterpart in the comparison spectrum. Based on theoretical reasoning, there is a total maximum loss by reflection equivalent to a sector opening of 0.04, for a cell such as the one used, but filled with water. The blackening of the comparison spectrum is too great by a certain amount, since its light has not suffered this loss, while the light sent through the absorption cell has, presumably at least; hence the absorption coefficient must be decreased by a certain figure. But it would not do to apply this correction without further consideration, for the conditions in the absorption cell are different from those in the blank cell. The reflection takes place mainly at two surfaces, at the front surface of the first plate and at the back surface of the rear plate; but in the absorption cell, the second surface receives less light than the first; in fact, near the point of complete absorption it receives practically none, so that the correction would be too large. Dividing the correction into two equal parts and applying it numerically in order to estimate its magnitude, the light reflected from the first surface requires a uniform correction for γ-pyridone of 3.3 $\times$ 1000, to be subtracted from the value of ϵ; this would be the largest correction for any one of the eight substances studied; and for chelidamic acid, a correction of 1.7 $\times$ 100 is required, also to be subtracted; this would be the smallest correction. Each curve would be lowered, but the change would not affect the value for persistence. The correction for the light reflected by the second quartz plate might be applied at a single point, at the head of the curve, at the point of maximum transmission, which would be lowered by the same amounts, respectively, that are given above for the two substances chosen as examples, and these amounts would again be the extreme values for the correction. This second correction would affect the value for persistence, but not to an amount sufficient to change the conclusions based on the uncorrected curves. It probably will be agreed that the considerations on which this estimate is based are correct enough to give the magnitude of the error, which for the values for persistence is then well within 4%. Too many uncertainties, however, are involved to warrant making the correction; the resulting values would still be in doubt. The error due to reflection is so close to the error due to the degree of the sensitiveness of the plate that its experimental verification is extremely difficult, and will require a long study; also, in setting the constant k equal to unity, in the expression $\log (t_1/t_0) = k \log (I_0/I_{tr})$, an uncertainty has been introduced, which requires further information. For these various reasons it is better to give the actual readings and the corresponding uncorrected values for the molecular extinction coefficient, but with full description of the arrangements.

Experimental Results

GROUP A

TABLE I

γ-PYRIDONE

Below the curve represents absorption, above, transparency.

Sector opening	Absorption begins at	Absorption ends at	Absorption begins at
0	complete	..	..
0.1	2795	..	..
.2	2725	2322	2270
.3	2690	2360	2250
.4	2660	2400	2235
.5	2636	2430	2225
.6	2615	2460	2210
.7	2600	2490	2200
.8	none	..	2195
.9	none	..	2190
1.0	none	..	2180

The final dilution was 0.0001196 *M*, the cell was 0.5 cm. and the plate constant 1.67.1 × 100.

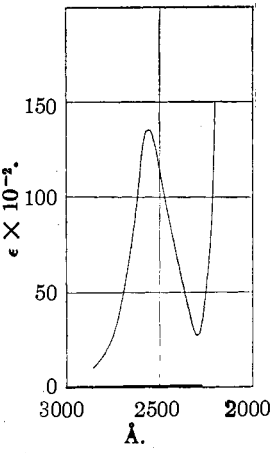


Fig. 1.—Upper curve: γ-pyridone. Lower curve: γ-hydroxy-piperidine.

TABLE II

N-METHYL-γ-PYRIDONE

Sector opening	Absorption begins at	Absorption ends at	Absorption begins at
0	complete	..	..
0.1	2830	2320	2226
.2	2770	2360	2205
.3	2752	2400	2195
.4	2740	2435	2187
.5	2725	2465	2175
.6	2705	2492	2165
.7	2690	2508	2160
.8	2675	2521	2155
.9	2655	2540	2150
1.0	2622	2580	2140

The final dilution was 0.0001203 *M*, the cell 0.5 cm. thick the plate constant 166.3 × 100.

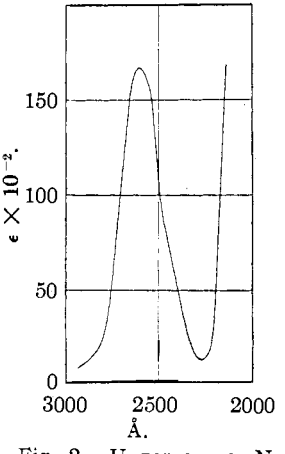


Fig. 2.—Upper curve: N-methyl-γ-pyridone. Lower curve: N-methyl-γ-hydroxy-piperidine.

TABLE III

γ-PYRONE

Sector opening	Absorption begins at	Absorption ends at	Absorption begins at
0	complete	..	..
0.1	complete	..	..
.2	2900	..	..
.3	2735	..	..
.4	2675	..	..
.5	2645	2250	2175
.6	2622	2282	2160
.7	2612	2322	2150
.8	2606	2360	2140
.9	2560	2380	2130
1.0	2550	2403	2120
1.1	2540	2458	2115
1.2	none	..	2112
1.3	none	..	2110

The final dilution was 0.000699 *M*, the cell 0.1 cm. and the plate constant 142.9 × 100.

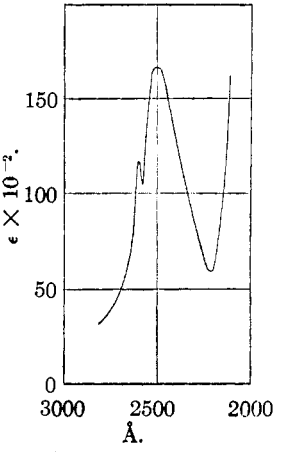


Fig. 3.—γ-Pyrone.

GROUP B

TABLE IV

CHELIDAMIC ACID

Sector opening	Absorption begins at	Absorption ends at	Absorption begins at
0	complete	..	..
0.1	3090	..	..
.2	3054	..	..
.3	3025	..	..
.4	2990	2460	2430
.5	2955	2540	2400
.6	2922	2600	2375
.7	2880	2654	2361
.8	2830	2726	2352
.9	none	..	2345

The final dilution was 0.0001185 *M*, the cell 1 cm., the plate constant 84.37 × 100.

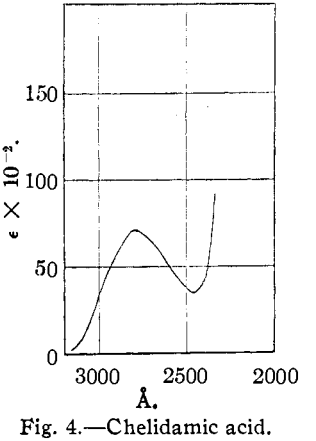


Fig. 4.—Chelidamic acid.

TABLE V

N-METHYL-CHELIDAMIC ACID

Sector opening	Absorption begins at	Absorption ends at	Absorption begins at
0	complete	..	..
0.1	2940	..	..
.2	2880	..	..
.3	2840	..	..
.4	2810	..	..
.5	2795	..	..
.6	2770	..	..
.7	2750	2475	2400
.8	2728	2520	2330
.9	2701	2551	2301
1.0	2640	2600	2280
1.1	none	..	2255

The final dilution was 0.0001715 *M*, the cell 0.5 cm., and the plate constant 116.62 × 100.

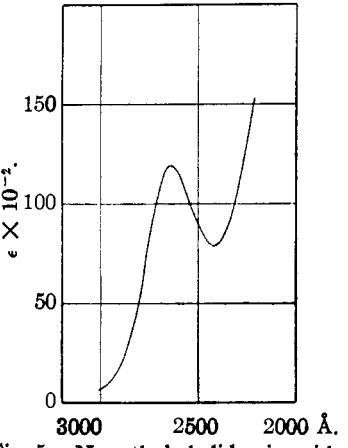


Fig. 5.—N-methyl-chelidamic acid.

TABLE VI

CHELIDONIC ACID

Sector opening	Absorption begins at	Absorption ends at	Absorption begins at
0	complete	..	..
0.1	3020	..	..
.2	2960	..	..
.3	2925	..	..
.4	2910	..	..
.5	2900	..	..
.6	2880	..	..
.7	2860	..	..
.8	2840	2485	2400
.9	2810	2520	2355
1.0	2795	2565	2340
1.1	2780	2600	2328
1.2	2750	2640	2310
1.3	none	..	2300

The final dilution was 0.0001103 *M*, the cell 1 cm. and the plate constant 90.67 × 100.

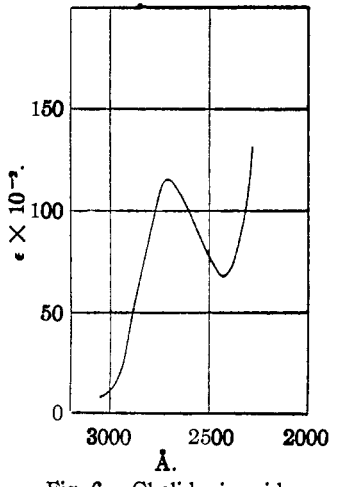


Fig. 6.—Chelidonic acid.

GROUP C

The preliminary trials showed that γ-hydroxy-piperidine has no selective absorption. Thus with a sector opening of 0.7 a cell thickness of 1 mm. and a dilution of 7.4, 1.85, 2.5 and 3.7 g. per liter, the absorption began at 2210, 2490, 2600 and 3160 Å., respectively.

Calculating the corresponding molecular extinction coefficients and plotting them on the same scale as those for the six preceding substances gave the lower curve in Table I.

TABLE VII

N-METHYL-γ-HYDROXY-PIPERIDINE

Sector opening	Absorption begins at	Absorption ends at	Absorption begins at	Sector opening	Absorption begins at	Absorption ends at	Absorption begins at
0	complete	..	..	0.7	2800	..	..
0.1	complete	..	..	.8	2770	..	..
.2	3200	..	..	.9	2740	..	..
.3	3040	..	..	1.0	2710	..	..
.4	2960	..	..	1.1	2690	2555	2405
.5	2890	..	..	1.2	none	..	2370
.6	2840	..	..	1.3	none	..	2340

The final dilution was 0.02959 *M*, the cell 1 cm. thick, and the plate factor 0.338 × 100; the curve is shown as the lower one with Table II. N-Methyl-γ-hydroxy-piperidine has almost no selective absorption.

Discussion of the Results

An inspection of the curves shows that the persistence for Group A is of the same order for the three members, and is considerable; the persistence for Group B is also of the same order for the members of this group, but it is only about one-third of that for the skeleton substances. The ring structures in Group C have practically no selective absorption. The values for persistence are grouped together in Table VIII.

TABLE VIII[9]

PERSISTENCE OF THE ABSORPTION BAND FOR THE THREE ACIDS, FROM ε/100 VALUES

Chelidamic	N-Methyl-chelidamic	Chelidonic	
71——35	119——79	116——68	
36——40——48			
	Av. persistence		41

PERSISTENCE OF THE ABSORPTION FOR THE NON-CARBOXYLATED SUBSTANCES FROM ε/100 VALUES

γ-Pyridone	N-Methyl-γ-pyridone	γ-Pyrone	
135——27	167——12	163——58	
108——155——105			
	Av. persistence		123

If we consider, with J. Stark[10] that the "loosened electron or its field of forces" is the seat of absorption, which may lie in the ultraviolet, it is reasonable to suppose that the substitution of two bulky carboxyl groups for two hydrogen atoms will interfere with the process of absorption (for instance, spatially, if electron swings are assumed), and the power of absorption per molecule will be less for the substituted ones than for the

[9] In this table we have taken the numerical difference between the values of the molecular extinction coefficient at the maximum and minimum in the curve, divided by 100; this differs from the values for persistence which are obtained from curves plotted with logarithms of relative thicknesses of the layer of solution in the cell, as ordinates.

[10] Stark, "Die Prinzipien der Atomdynamik," S. Hirzel, Leipzig, 1911, vol. 2, pp. 116–122.

unsubstituted ones; and on dilution, the absorption will die out sooner, in other words, the persistence will be lower.

According to Hartley's theory of color, weighting the molecule should cause a shift of the absorption band toward the red end of the spectrum. The shifts observed are listed in Table IX; chelidonic acid and chelidamic acid have a band nearer the red end than pyrone and γ-pyridone, respectively, and by the same amount; to that extent our results agree with this theory. N-Methyl-chelidamic acid has a band which is also nearer the red end than its skeleton substance, N-methyl-γ-pyridone, but by a very small amount only.

TABLE IX

SHIFT MEASURED FROM THE HEAD OF THE CURVE, LAST AND HIGHEST VALUE OF MOLECULAR EXTINCTION COEFFICIENT FOR FIRST ABSORPTION CONE

Chelidamic acid or di-carboxylic γ-pyridone	2780 shift toward the red	γ-pyridone	2550 Å. 230 Å.
Chelidonic acid or di-carboxylic γ-pyrone	2700 shift toward the red	γ-pyrone	2490 Å. 210 Å.
N-Methyl-chelidamic acid or di-carboxylic N-methyl-γ-pyridone	2630 shift toward the red	N-methyl-γ-pyridone	2600 Å. 30 Å.

As to the effect on the position of the band by the replacement within the ring structure of O by NH or NCH_3, the results are conflicting; the effect is not the same in the two groups.

	Placement of the head of the curve Group A	Group B
O (16) replaced by NH (15)	60 Å. toward red	80 Å. toward red
NH (15) replaced by NCH_3 (29)	50 Å. toward red	150 Å. away from red

The theory of Hartley is not meant for changes within the ring, and consequently the results above have no bearing on it; it is evident that in a ring structure, the field of forces exerted by various groups will be as important as mere weight, if not more so, in determining the position of the absorption bands.

Materials

In the preparation of the materials, special caution was observed to prevent contamination of one substance by another; to that end, new glassware was used freely; no attention was paid to yield, only to purity; charcoal was not used to remove traces of color.

Chelidonic acid was synthesized from ethyl oxalate and acetone by the action of sodium alcoholate in alcohol followed by neutralization in 10% hydrochloric acid. The ester was reslurried, and washed repeatedly with acidulated ice water until only faintly yellow; it was saponified in concd. hydrochloric acid, the acid filtered off, reslurried, and washed until practically white. The non-volatile matter was 0.3%, the melting point the same as found by Willstätter and Pummerer.[11] It was desiccated at 160°.

γ-Pyrone was prepared by the distillation of chelidonic acid, which had been

[11] Willstätter and Pummerer, *Ber.*, **37**, 3744 (1904).

previously desiccated at 160°, and purified by redistillation at low pressure, twice; the boiling point was 119° (35 mm.); it solidified in cold water to form large, colorless crystals which melted at 32°, in agreement with the tables.

Chelidamic acid was made from the chelidonic acid obtained as described above by dissolving it in concd. ammonium hydroxide and refluxing the solution for five hours, with occasional additions of ammonium hydroxide; after the mixture had been neutralized, the acid was filtered off, washed and dissolved once more in ammonium hydroxide and refluxed a second time; this was followed by acidification, filtering and washing; the white powder resulting was used as such; the decomposition point, determined by means of the usual melting-point tube, was found to be the same that was reported by H. Meyer,[12] 248°.

γ-Pyridone was made by heating chelidamic acid, previously desiccated at 120° at atmospheric pressure until the evolution of carbon dioxide ceased, and distilling the residue at low pressure; it was purified by two distillations at low pressure. It is a colorless solid, melting above 120°; its boiling point, 257–260° (10 mm.) distinguishes it readily from the reduced substance described below.

γ-Hydroxy-piperidine was made by reducing the γ-pyridone with sodium and alcohol, following the directions of Emmert.[13] The reduced base was isolated and purified by distillation at low pressure; then it was distilled at atmospheric pressure when it was found to have the right boiling point, about 210°. A second reduction was performed without changing the constants. γ-Hydroxy-piperidine is also a solid, melting at 86° (confirmed), forming large aggregates but no separate crystals; some piperidine was obtained in the first fractions.

N-Methyl-chelidamic acid was prepared by the method of Haitinger and Lieben,[14] which consists of heating under pressure chelidonic acid in a water solution of methylamine; by means of a large excess of methylamine and an extra long heating period, complete conversion was insured. The methylamine used was made from methylamine hydrochloride twice crystallized from absolute alcohol to exclude ammonia. On acidifying, the acid separates in grainy crystals, very different from those of either chelidonic or chelidamic acid. After a washing the color was nearly white; the nonvolatile matter was 0.3%; m. p.,[15] 197–200°.

N-Methyl-γ-pyridone was prepared by heating N-methyl-chelidamic acid at atmospheric pressure until all of the carbon dioxide had passed out, then distilling the residue at reduced pressure; two such distillations gave a pure product, solidifying to aggregates of large crystals, colorless or cream-colored, melting at 89° essentially in agreement with the literature.[16]

N-Methyl-γ-hydroxy-piperidine was made by reducing N-methyl-γ-pyridone with sodium and alcohol; after the reduced base had been isolated (by means of its hydrochloride), it was purified by distillation; it boils at 116–118° (36 mm.) and is a liquid at room temperature.[17]

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[12] Meyer, *Monatsh.*, **24**, 204 (1904).

[13] Emmert and Dorn, *Ber.*, **48**, 687 (1915); this paper also gives directions for preparing the γ-pyridone.

[14] Haitinger and Lieben, *Monatsh.*, **6**, 293 (1885).

[15] Haitinger and Lieben, Ref. 14, merely state that it decomposes above 180°.

[16] Haitinger and Lieben give the melting point as "above 89°," Ref. 14, p. 293.

[17] An extended study of this substance, and of the two preceding ones has been in progress at this Laboratory by Mr. F. Zwilgmeyer and one of the present authors (E. R. R.) and is nearly completed; it will be reported as soon as possible; it is from this work that the samples for the study of the absorption of the three methylated compounds were taken.

The hydrochloride may be precipitated by adding anhydrous alcoholic hydrogen chloride to the base dissolved in acetone.

Anal. Subs., 0.5715. Calcd. for $C_6OH_{13}N.HCl$: Cl, 23.40. Found: 23.48.

The quartz spectroscope and sector photometer used in this work form part of the equipment of the New York State Institute for the Study of Malignant Diseases, at Buffalo; permission to use the instruments was secured through the courtesy of the physicist of the Institute, Dr. K. Wilhelm Stenström, to whom we are also indebted for valuable advice.

Summary

1. The absorptions in the near ultraviolet region (to 2100 Å.) of γ-pyridone, N-methyl-γ-pyridone, γ-pyrone (Group A), chelidamic acid, N-methyl-chelidamic acid, chelidonic acid (Group B), γ-hydroxy-piperidine, N-methyl-γ-hydroxy-piperidine (Group C), have been studied and recorded.

2. Curves have been plotted by means of the molecular extinction coefficient as abscissa, the wave length as ordinate; from these curves the persistence is obtained.

3. Group A and Group B show selective absorption; the persistence for Group A is three times as great as that for Group B. Group C has only very slight selective absorption.

4. The curves for Group B are shifted toward the red, when compared to Group A; this shift is due to the introduction of two carboxyl groups into the uncarboxylated molecule, and is in agreement with the rule of Hartley. For two members, the shift is considerable; for one, it is slight.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

TRIPHENYLMETHYL. XXXV. HALOGEN-SUBSTITUTED ACRIDYLS. THE REACTIVITY OF THE HALOGEN IN THEM

BY M. GOMBERG AND D. L. TABERN[1]

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In previous papers the theory has been advanced that triarylmethyls possess their property of selective absorption in the visible spectrum not merely because of the trivalent carbon atom in them, but rather in virtue of the quinoidation of the free radical. In support of this view we have: (1) the depth of color is not directly proportional to the amount of the monomolecular free radical in solution; (2) the triarylmethyls contain a benzene nucleus which evidences a degree of reactivity wholly unusual in an ordinary benzene ring. Thus, *p*-bromotriphenylmethyl, in complete

[1] The material here presented is from the dissertation submitted by D. L. Tabern to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1924.