residual liquid was favorable to reaction (140°) where it was maintained for seven hours. In working up the mixture in the usual way, 30 cc. (0.36 mole) of hydrochloric acid was required for neutralization, indicating that 36% of the sodioethylmalonate still had not reacted; yield 125.5 g. (41%), b.p. 140–145° (1 mm.).

Anal. Calcd. for $C_{18}H_{26}O_4$: C, 70.5; H, 8.6. Found: C, 70.2; H, 8.3.

5-Ethyl-5-(β-phenylpropyl)-barbituric Acid.—The above ester (26.0 g., 0.084 mole) and 9.2 g. (0.152 mole) of urea were refluxed six hours in a solution of sodium ethoxide prepared from 5.2 g. (0.228 mole) of sodium and 100 cc. of absolute alcohol. The yield of crude acid was 18.0 g. (79%). The pure acid (13.5 g.) was obtained by crystallization from 50 cc. of toluene; m.p. 155–156°.

Anal. Calcd. for $C_{15}H_{18}O_3N_2$: N, 10.2. Found: N, 9.9.

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Lactam of N-(β-Aminoethyl)-chelidamic Acid—A Pyridopiperazine Ring[1]

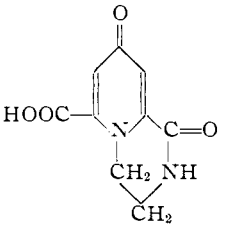
BY A. W. SCHWAB

RECEIVED OCTOBER 2, 1953

Chelidamic acid is a tridentate molecule which has proved to be an excellent metal-inactivating agent for vegetable oil systems.[2] Because chelidamic acid is easily prepared from chelidonic acid and ammonia,[3] it was thought that chelidonic acid and ethylenediamine might give 1,1′-ethylene-bis-[2,6-dicarboxy-4-pyridone]. This compound would be sexadentate and would be expected to have unusual metal-chelating properties.

Campbell and his co-workers have prepared γ-pyridones simply by the addition of an aqueous solution of the γ-pyrone to an aqueous solution of the amine.[4] Previously, Armit and Nolan had prepared this type of compound in alcohol solution.[5] Freeman, Ringk and Spoerri also used alcoholic solutions for the preparation of N-aralkyl derivatives of 4-pyridone and chelidamic acid.[6] Prior to this, N-substituted chelidamic acids were prepared by the method of Haitinger and Lieben.[7]

It was found that the addition of ethylenediamine to a hot ethanol solution of chelidonic acid gave an insoluble salt. This compound appears to be the salt of equimolar amounts of chelidonic acid and ethylenediamine. When an aqueous solution is treated with hydrochloric acid, an insoluble precipitate settles out which analysis indicates to be compound I. This lactam is bidentate and shows only slight metal-inactivating properties compared with chelidamic acid.[8]



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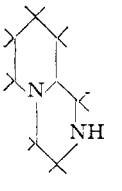

II

This lactam I or the basic ring system II to which it belongs has not been reported. Based on the aromatic system, compound I might be named as a pyridopiperazine derivative, but a simpler name would be the lactam of N-(β-aminoethyl)-chelidamic acid. Using the azabicycloalkane system, compound II is named 1,4-diazabicyclo(4.4.0)decane.

Experimental

Ethylenediamine Chelidonic Acid Salt.—Seven grams of ethylenediamine (95%) was added dropwise to a refluxing ethanol solution containing 7.0 g. of chelidonic acid. Upon addition of the first drop of ethylenediamine, a precipitate settled out, and this insoluble compound continued to form as more and more ethylenediamine was put in. The solution was refluxed for 2 hours after the addition of the ethylenediamine. It was then cooled, and the insoluble product was filtered off. Recrystallization from water produced large colorless needles. These needles were filtered off and then dried over phosphorus pentoxide in a vacuum desiccator. The yield was approximately 4.0 g., m.p. 239–240° (dec.). The salt was neutral to *p*H indicator paper, and was hygroscopic. Additional quantities of the salt were obtained by concentrating the filtrates. Analysis showed the compound to have the composition of equimolar amounts of chelidonic acid and ethylenediamine.

Anal. Calcd. for $C_9H_{12}O_6N_2$: C, 44.3; H, 4.92; N, 11.5. Found: C, 44.2; H, 4.92; N, 11.7.

Lactam of N-(β-Aminoethyl)-chelidamic Acid.—When a saturated aqueous solution of the ethylenediamine salt of chelidonic acid was treated with dilute hydrochloric acid, an insoluble precipitate settled out. This precipitate was filtered and washed with ice-water. It was dried over phosphorus pentoxide in a vacuum desiccator. This compound did not melt below 300°. It was acid to *p*H paper and had a neutral equivalent of 208 (theory 208). The ultraviolet absorption spectrum of a 0.00012 *M* solution of this compound in 0.01 *N* sodium hydroxide showed a peak at 232 mμ with ε 19000 and a shallow peak at 272 mμ with ε 7700. These data were found to be consistent with the spectra of closely related substances.[3,9,10]

The infrared spectrum was determined using powdered potassium bromide and sample in a pressed disk[11] with a Perkin–Elmer, Model 21, Infrared Spectrograph and is given in Fig. 1. It is to be observed that there is a single sharp band at 3.09 μ which is evidence of the presence of a substituted amide.[12] No doublet was observed in this region which might indicate the primary amine group. Peaks were observed at 5.84 and 5.90 μ which could indicate the presence of the carbonyl and amide groups, respectively. A peak at 6.12 μ might be attributed to the presence of a zwitterion.[13] Before complete confirmation could be obtained through infrared investigations, it would be necessary to compare spectra of a number of known and new compounds of similar structure.

Anal. Calcd. for $C_9H_8O_4N_2$: C, 51.9; H, 3.85; N, 13.5. Found: C, 51.1; H, 3.93; N, 13.4.

The *p*-bromophenacyl derivative crystallized with 2 molecules of water and melted at 172–174° with charring.

(1) From one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted. This paper is based on some work submitted by A. W. Schwab in partial fulfillment of the requirements for the Ph.D. Degree at Bradley University, Peoria, Illinois.

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Anal. Calcd. for $C_{17}H_{13}O_5N_2Br$: C, 50.4; H, 3.21; N, 6.91; Br, 19.75. Found: C, 50.3; H, 3.25; N, 6.79; Br, 20.1.

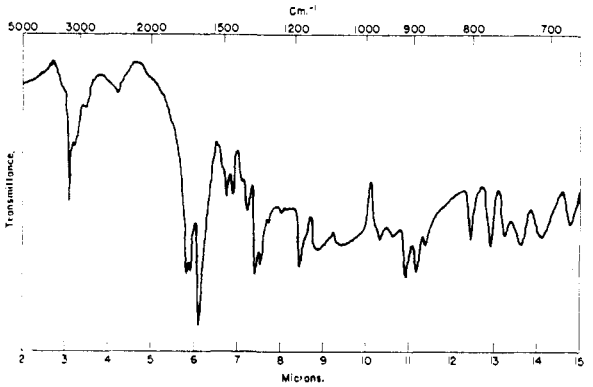

Fig. 1.—Lactam of N-(β-aminoethyl)-chelidamic acid.

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Hydrogen Bonding in Phenolic Resin Intermediates

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The properties of phenolic resins might be expected to be peculiarly influenced by hydrogen bonding, for these resins contain many hydroxyl groups particularly subject to such bonds. Indeed hydrogen bonds often have been postulated[2] as an explanation for the peculiarities in behavior of certain phenolic intermediates. So far, however, we lack sure knowledge of the position, nature, effect, and even of the existence of such bonds. This paper is intended to present certain facts concerning hydrogen bonding in the field of novolac-type, phenolic resins.

In the course of some titrations of carboxylic acids in presence of low molecular weight phenolic resins it was noted that the presence of some acid weaker than the carboxylic interfered with the end-points of the latter. The parent phenol itself proved not to be responsible for this effect. Therefore a study of the acidity of other intermediates possibly present in the mixture was made.

A titration system suitable for this study was found in anhydrous ethylenediamine,[3] using an ethylenediamine solution of sodium (*p*-aminoethoxide) as titrant and recording the potential between two Sb electrodes, one in the titrant and one in the titration vessel. In this system carboxylic acids and all phenols, including so-called "pseudo-phenols," can be titrated easily. Examination of a series of compounds containing two phenolic nuclei linked in various ways by this means showed that the acidity of various *o*-dibenzyl ethers (I), diphenylethanes (II and III) and *p*-diphenylmethanes (IV and V) does not deviate very much from that of a simple phenol (Fig. 1). Also, as was to be expected, the two hydroxyls present in these compounds do not differ appreciably in acidity. The titration curve of various *o*-diphenylmethanes (VI), however, showed a very sharp break after addition of sufficient alkali to neutralize only one of the two hydroxyls, and little or no indication of the other.

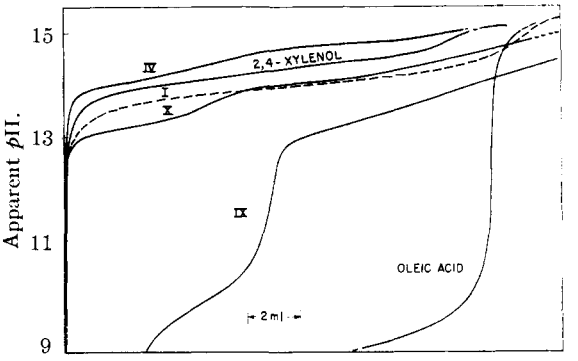
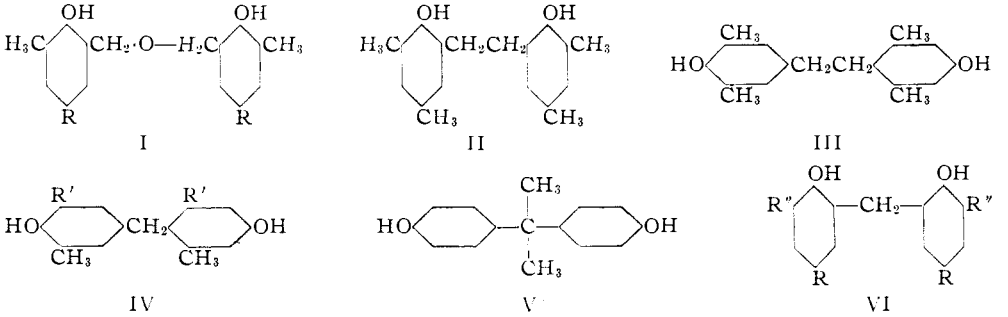


Fig. 1.—Titrations in isopropyl alcohol–benzene 1:1.

This seemingly somewhat unusual result was corroborated by titration in benzene–isopropyl alcohol system[4] against glass–calomel electrodes. Results in this latter system are more reproducible



R = $-CH_3$ or $-C(CH_3)_3$, R′ = $-CH_3$ or $-CH_2OH$, R″ = $-H$ or $-CH_3$

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