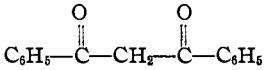
any case, the absorption between 4.3 and 4.9 μ can be attributed to deuterium bonds.

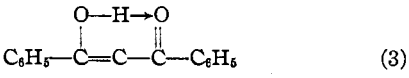
The lower dibasic acids were quite insoluble in carbon tetrachloride, but diethylmalonic and azelaic acids were sufficiently soluble to get the curves shown in Fig. 4. These curves are quite similar to the one for propionic acid. The abnormal heights of the 3.33 and 3.38 μ maxima are due, as for propionic acid, to the superposition of CH absorption upon that for the hydrogen bonds. The dibasic acids offer the possibility of forming monomolecular hydrogen bonded rings as well as dimers or even polymers. Unfortunately the data are not sufficient to tell precisely what is taking place, except that considerable hydrogen bonding does occur.

From the formulas for dibenzoylmethane ($C_6H_5COCH_2COC_6H_5$), diphenylmethane ($C_6H_5CH_2C_6H_5$) and benzil ($C_6H_5COCOC_6H_5$), one would expect certain similarities in their absorption spectra. All three compounds give the characteristic aromatic CH absorption in the neighborhood of 3.24 μ. The aliphatic CH absorption for diphenylmethane is easily accounted for,[7] but the broad absorption of the dibenzoylmethane near 3.8 μ needs some other explanation. It is evident that the aliphatic hydrogens of the conventional structure



(2)

have undergone some change. A plausible explanation is that advanced by Hilbert, Wulf, Hendricks and Liddel,[3] who suggested enolization followed by hydrogen bonding to give the structure



(3)

Since no fundamental OH absorption is observed, the hydrogen bonding of the enol must be complete. Benzil, on the other hand, cannot enolize and accordingly does not show the same absorption.

The authors are indebted to Professors W. H. Rodebush and A. M. Buswell for helpful suggestions and criticism.

Summary

The infrared absorption spectra for ordinary and deuterated acetic, benzoic and propionic acid have been investigated in the "hydrogen bond" region and the results interpreted on the basis of their structures. Likewise the absorption for diethylmalonic and azelaic acids has been studied and discussed. Infrared absorption measurements for dibenzoylmethane (and related molecules) suggest that dibenzoylmethane undergoes enolization followed by hydrogen bonding.

URBANA, ILLINOIS RECEIVED AUGUST 7, 1939

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

The Structure of Monocrotaline, the Alkaloid in *Crotalaria Spectabilis* and *Crotalaria Retusa*. I

BY ROGER ADAMS AND E. F. ROGERS

Crotalaria is a genus of leguminous plants, many species of which are commonly used in the southern part of the United States as soil-enriching legumes. *Crotalaria spectabilis* is perhaps the most important. Like many species of *Crotalaria* it is toxic and its toxicity has been shown to be due to an alkaloid monocrotaline.[1a] The same alkaloid has now been found also in the seed of the *Crotalaria retusa*.[1b]

(1) (a) Neal, Rusoff and Ahmann, THIS JOURNAL, **57**, 2560 (1935). (b) Greshoff, *Ber.*, **23**, 3537 (1890). The *Crotalaria spectabilis* strain grown in Florida and southern Georgia is toxic to chickens and larger animals. On the other hand, in South Carolina the seed of the early strain of *Crotalaria spectabilis* is non-toxic to blackbirds and partridge. Whether these birds are resistant to the alkaloid or whether the strain as grown in South Carolina contains no alkaloid or a different non-toxic alkaloid is now being studied.

Neal, Rusoff and Ahmann[1a] extracted monocrotaline from crushed seed by means of aqueous ammonia and reported a tentative formula of $C_{16}H_{26}O_6N$. The extraction proceeded much more smoothly, however, and the yields were improved several fold if ethanol was used as a solvent. A careful analysis of pure monocrotaline, its hydrochloride and methiodide revealed the molecular formula to be not that previously suggested but $C_{16}H_{23}O_6N$. Such a formula resembles closely those of the *Senecio*, *Heliotropium* and *Trichodesma* alkaloids, characteristic for which is alkaline hydrolysis to an acid and an alkanolamine. Hydrolysis of monocrotaline confirmed this supposition for cleavage yielded a basic product

which proved to be retronecine, the base obtained by hydrolysis of several of the *Senecio* alkaloids and an acid, $C_7H_{12}O_3$, monocrotic acid.

$$C_{16}H_{23}O_6N + H_2O(BaO_2H_2) \longrightarrow C_8H_{13}O_2N + C_7H_{12}O_3 + [CO_2]$$

From the above equation, it is obvious that carbon dioxide has been lost in the reaction due, presumably, to decomposition of the acid present in the monocrotaline.

Another mode of cleavage[2] successful on analogous alkaloids has been by hydrogenolysis. In those alkaloids previously studied which gave retronecine on hydrolysis, reduction gave retronecanol which has one less hydroxyl than retronecine and no olefin linkage. The acid part of the molecule unless containing an olefin linkage remained unaffected. Monocrotaline was readily reduced to retronecanol and an acid which will be designated as monocrotalic acid since it is presumably the acid present in the form of an ester in the alkaloid.

$$C_{16}H_{23}O_6N + 2H_2 \longrightarrow C_8H_{15}ON + C_8H_{12}O_5$$

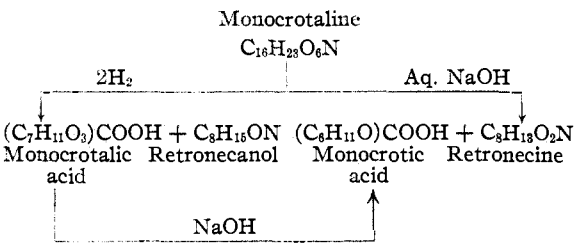
A mixed melting point of retronecine from monocrotaline with authentic retronecine, kindly furnished by Dr. R. H. F. Manske, gave no depression. A table showing the properties of retronecine and retronecanol from monocrotaline in comparison with those of the bases isolated from other sources is given below.

TABLE I

CONSTANTS ON ALKANOLAMINES FROM MONOCROTALINE

Alkanolamine	M. p., °C.	Rot. $[\alpha]_D$	Alkanolamines from monocrotaline M. p.	Rot.	Solvent for rotation
Retronecine[2b]	121–122	+50.2	121	+49.3	Ethanol
Retronecine hydrochloride[2b]	161	−16.0	161–162	−15.4	Ethanol
Retronecine diac. picrate[2b]	146		146		
Retronecanol[3]	98–99 (92–93)		95–96	−91.1	Ethanol
Retronecanol hydrochloride			210		
Retronecanol methiodide[2b]			193	−52.8	Methanol
Retronecanol picrate	208 (211)		210		

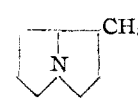
Monocrotalic acid is optically active. Direct titration indicates it to be monobasic but by addition of excess alkali and back titration, a higher neutral equivalent is found, strongly indicating the presence of a lactone linkage. It forms a *p*-bromophenacyl ester. By heating monocrotalic acid with alkali, decomposition occurs and a liquid monobasic acid, $C_7H_{12}O_3$, monocrotic acid, results. This acid is identical with that obtained by alkaline hydrolysis of the original alkaloid. It is optically inactive, monobasic, and forms a *p*-bromophenacyl ester. The transformations just discussed may be tabulated



The structure of the $C_6H_{10}O$ residue in monocrotic acid is now being studied.

The acid portions of the *Senecio*, *Heliotropium*, and *Trichodesma* alkaloids have received very limited examination. The facts that are known about them, however, lead us to believe that it is doubtful whether they are so dissimilar in constitution as expressed by a reviewer of the work in this field.[4] The acids are unknown in structure except *dl*-lactic acid, which is probably a degradation product of the acid occurring in the alkaloid trichodesmine, and angelic acid which is possibly a degradation product of the acid occurring in the alkaloid lasiocarpine.

The knowledge of the most commonly occurring base, retronecine, or the other very closely related bases is still limited. Menshikov[2a,5] has established the probable structure of the nucleus present in these bases as a methylpyrrolizidine



but no evidence is as yet available which will place the hydroxyls and olefin linkage.

A large number of alkaloids with different acids and identical or very similar bases has been shown to occur in four genera of plants, the *Senecio*, *Trichodesma*, *Heliotropium* and recently *Erechtites* to which must now be added a fifth genus, the *Crotalaria*. The relationship between the alkaloids now known is shown in the following table.

(2) (a) Menshikov, *Ber.*, **68**, 1051 (1935); (b) Barger, Seshadri, Watt and Yabuta, *J. Chem. Soc.*, 11 (1935).

(3) (a) Menshikov and Rubinstein, *Ber.*, **68**, 2039 (1935); (b) Konovalova and Orekhov, *Bull. soc. chim.*, [5] **4**, 1285 (1937).

(4) Haworth, *Ann. Reports Chem. Soc. London*, 329 (1938).

(5) Menshikov and co-workers, *Ber.*, **65**, 974 (1932); **66**, 875 (1933); **68**, 1555 (1935); **69**, 1799, 1802 (1936); *J. Gen. Chem.* (*U. R. S. S.*), **7**, 1632 (1937); *Bull. Acad. Sci.* (*U. R. S. S.*) *Classe Sci. Math. Ser. Chim.*, **5**, 1035 (1937).

TABLE II

KNOWN ALKALOIDS OF THE ACID-ALKANOLAMINE TYPE

	Alkaloid	Alkanolamines	Acid
Crotalaria			
spectabilis[1a]	Monocrotaline, $C_{16}H_{23}O_6N$	Retronecine, $C_8H_{13}O_2N$	Monocrotalic, $C_8H_{12}O_5$
retusa[1b]	Monocrotaline, $C_{16}H_{23}O_6N$	Retronecine, $C_8H_{13}O_2N$	Monocrotalic, $C_8H_{12}O_5$
Trichodesma incanum[3a]	Trichodesmine, $C_{18}H_{27}O_6N$	Retronecine	*dl*-Lactic and isobutyl methyl ketone
Senecio			
cineraria[6]	Jacobine, $C_{18}H_{25}O_6N$	Retronecine	Jaconecic, $C_{10}H_{16}O_6$
jacobaea[6a,7]	Jacobine, $C_{18}H_{25}O_6N$	Retronecine	Jaconecic, $C_{10}H_{16}O_6$
	Jaconine, $C_{18}H_{25}O_6N$	.....	.....
	Jacodine, $C_{18}H_{25}O_5N$	.....	.....
aquaticus[6b]	Jacodine, $C_{18}H_{25}O_5N$	.....	.....
vulgaris[8]	Senecine, ...	.....	.....
	Senecionine, $C_{18}H_{25}O_5N$	Retronecine	Senecic, $C_{10}H_{14}O_4$
viscosus[8b]	Senecionine, $C_{18}H_{25}O_5N$	Retronecine	Senecic, $C_{10}H_{14}O_4$
aureus[6a,7a,13,14]	Senecionine, $C_{18}H_{25}O_5N$	Retronecine	Senecic, $C_{10}H_{14}O_4$
squalidus[8b]	Senecionine, $C_{18}H_{25}O_5N$	Retronecine	Senecic, $C_{10}H_{14}O_4$
	Squalidine, $C_{18}H_{25}O_5N$	Retronecine	Squalinecic, $C_{10}H_{14}O_4$ or $C_{10}H_{18}O_5$
stenocephalus[9]	Seneciphylline, $C_{18}H_{23}O_5N$	Retronecine	Seneciphyllic, $C_{10}H_{14}O_5$
platyphyllus[9,10]	Seneciphylline, $C_{18}H_{23}O_5N$	Retronecine	Seneciphyllic, $C_{10}H_{14}O_5$
	Platyphylline, $C_{18}H_{25}O_5N$	Platynecine, $C_8H_{15}O_2N$	Platynecic, $C_{10}H_{14}O_4$
retrorsus[2b,7a]	Retrorsine, $C_{18}H_{25}O_6N$	Retronecine	Retronecic, $C_{10}H_{16}O_6$
glaberrimus[6b]	Retrorsine, $C_{18}H_{25}O_6N$	Retronecine	Retronecic, $C_{10}H_{16}O_6$
venosus[6b]	Retrorsine, $C_{18}H_{25}O_6N$	Retronecine	Retronecic, $C_{10}H_{16}O_6$
isatideus[6b]	Retrorsine, $C_{18}H_{25}O_6N$	Retronecine	Retronecic, $C_{10}H_{16}O_6$
	Isatidine, $C_{18}H_{25}O_7N$	Isatinecine, $C_8H_{13}O_3N$	Isatinecic, $C_{10}H_{16}O_6$
erucifolius[6b]	....., $C_{18}H_{27}O_5N$	.....	.....
palustris[6b]	....., $C_{18}H_{27}O_5N$	.....	.....
latifolius[2b,11]	Senecifoline, $C_{18}H_{27}O_8N$	(Senecifolinine, $C_8H_{11}O_2N$)?	Senecifolic, $C_{10}H_{16}O_6$
	Senecifolidine, $C_{18}H_{25}O_7N$	.....	.....
mikanoides[8a]	Mikanoidine, $C_{21}H_{29}O_6N$	(Mikanecine, $C_8H_{15}O_2N$)?	Mikanecic acid, $C_{13}H_{16}O_5$
Heliotropium			
lasiocarpum[2a,5,12]	Heliotrine, $C_{16}H_{27}O_5N$	Heliotridine, $C_8H_{13}O_2N$	Heliotrinic, $C_8H_{16}O_4$
	Lasiocarpine, $C_{21}H_{33}O_7N$	Heliotridine, $C_8H_{13}O_2N$	Lasiocarpinic, $C_8H_{16}O_5$ and angelic

Experimental

Extraction of Monocrotaline from *Crotalaria spectabilis*.—Two kilograms of Florida grown *Crotalaria spectabilis* seed ground to 16-mesh was extracted continuously for seventy-two hours with 95% ethanol. The green-black solution was acidified to congo paper with citric acid, the solvent removed *in vacuo*, and the residue taken up in 400 cc. of water. The suspended fat was extracted with successive portions of ether until the ether extracts were colorless, then with two 100-cc. portions of chloroform. The aqueous solution was now treated with 200 cc. of chloroform and saturated aqueous sodium carbonate solution added with shaking, until the solution was distinctly alkaline to litmus. The color of the solution during this operation changes from a dull yellow-brown to a golden-yellow. The alkaloid was then extracted with two additional portions of 200 cc. and three portions of 100 cc. of chloroform. The combined chloroform extracts were evaporated to dryness *in vacuo* and the crude alkaloid obtained as a yellowish-white crystalline mass. It was purified by two crystallizations from absolute ethanol: white prisms, m. p., 197–198° (corr.) with decomposition; yield, 65 g. (3.2%).

Anal. Calcd. for $C_{16}H_{23}O_6N$: C, 59.06; H, 7.12; N, 4.30. Found: C, 59.14, 59.16; H, 7.05, 7.17; N, 4.42, 4.36.

Rotation. 0.5054 g. made up to 10 cc. in chloroform at 26°. α_D −5.54; *l*, 2; $[\alpha]^{26}D$ −54.7°.

The alkaloid does not react with nitrous acid. Methylimide and methoxyl determinations were negative.

No evidence indicating the presence of any other alkaloid could be secured either by fractional crystallization from absolute ethanol or fractional neutralization and extraction of a hydrochloric acid solution of the alkaloid.

Monocrotaline Hydrochloride.—The base was dissolved in ethanol and neutralized to congo paper with dilute hydrochloric acid. The solution was then evaporated to dryness, the hydrochloride taken up in the minimum

(6) (a) Barger and Blackie, *J. Chem. Soc.*, 584 (1937); (b) Blackie, *Pharm. J.*, **138**, 102 (1937).

(7) (a) Manske, *Can. J. Research*, **5**, 651 (1931); (b) Hosking and Brandt, *New Zealand J. Sci. Tech.*, **17**, 638 (1936).

(8) (a) Manske, *Can. J. Research*, **14**, 6 (1936); (b) Barger and Blackie, *J. Chem. Soc.*, 743 (1936); (c) Grandval and Lajoux, *Compt. rend.*, **120**, 1120 (1895); *Bull. soc. chim.*, [3] **13**, 942 (1895).

(9) Konovalova and Orekhov, *ibid.*, [5] **4**, 2037 (1937).

(10) Orekhov and Tiedebel, *Ber.*, **68**, 650 (1935); Orekhov, Konovalova and Tiedebel, *ibid.*, **68**, 1886 (1935).

(11) Watt, *J. Chem. Soc.*, **95**, 466 (1909).

(12) Menshikov and Shdanovich, *Ber.*, **69**, 1110 (1936).

(13) Manske, *Can. J. Research*, **17B**, 1 (1939).

(14) Manske, *ibid.*, **17B**, 8 (1939).

amount of hot methanol and ether added to turbidity. On cooling, the product crystallized: white prisms, m. p. 184° (corr.) with decomposition.

Anal. Calcd. for $C_{16}H_{23}O_6N\cdot HCl$: C, 53.11; H, 6.69; Cl, 9.79. Found: C, 53.22; H, 6.69; Cl, 9.87.

Rotation. 1.30 g. made up to 25 cc. in water at 28°. α_D −4.00; *l*, 2; $[\alpha]^{28}D$ −38.4°.

Monocrotaline Methiodide.—To a solution of 1 g. of monocrotaline in 10 cc. of chloroform and 1 cc. of methanol was added 2 cc. of methyl iodide. The oily methiodide which separated crystallized on cooling. Recrystallization from methanol–chloroform gave white prisms, m. p. 205° (corr.) with decomposition.

Anal. (Dried *in vacuo*.) Calcd. for $C_{16}H_{23}O_6N\cdot CH_3I$: C, 43.69; H, 5.61; I, 27.16. Found: C, 43.62; H, 5.54; I, 27.02. (Undried.) Calcd. for $C_{16}H_{23}O_6N\cdot CH_3I\cdot 3CH_3OH$: CH_3OH, 17.07. Found: CH_3OH, 17.11.

Rotation. (Dried sample.) 0.310 g. made up to 10 cc. in methanol at 28°. α_D +1.45; *l*, 2; $[\alpha]^{28}D$ +23.4°.

Extraction of Monocrotaline from *Crotalaria retusa*.—Extraction of 200 g. of *Crotalaria retusa* seed by the procedure described above for isolation of monocrotaline from *Crotalaria spectabilis* gave 3.77 g. (1.89%) of product, recrystallized from absolute ethanol. It proved to be monocrotaline as shown by m. p. 197–198° with decomposition, and rotation, as well as by the melting points of the hydrochloride, 185°, and of the methiodide, 205°.

Anal. (Base.) Calcd. for $C_{16}H_{23}O_6N$: C, 59.06; H, 7.12; N, 4.30. Found: C, 58.89; H, 7.05; N, 4.20.

Rotation. 1.05 g. made up to 25 cc. in chloroform at 28°. α_D −4.68; *l*, 2; $[\alpha]^{28}D$ −55.7°.

Anal. (Hydrochloride.) Calcd. for $C_{16}H_{23}O_6N\cdot HCl$: Cl, 9.79. Found: Cl, 9.80. (Methiodide.) Calcd. for $C_{16}H_{23}O_6N\cdot CH_3I$: I, 27.16. Found: I, 26.89.

Alkaline Hydrolysis of Monocrotaline

A. Monocrotic Acid, $C_7H_{12}O_3$.—A mixture of 20 g. of monocrotaline and 40 g. of barium hydroxide octahydrate in 250 cc. of water was refluxed for one hour. After cooling, the solution was saturated with carbon dioxide and the barium carbonate filtered. The filtrate was made just acid to congo and then submitted to continuous extraction with ether for twelve hours. The ether extract was dried over anhydrous sodium sulfate, the ether removed, and the residue distilled *in vacuo*. A second distillation gave a pure product, b. p. 145–146° (18 mm.); $n^{17.5}D$ 1.4449; d^{26}_4 1.072; yield, 4.2 g. (48%).

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39: Found: C, 58.26; H, 8.37.

The neutral equivalent of this product always ran from 5–7% high for a monobasic acid. Undoubtedly this was due to presence of a few per cent. of anhydro compound formed during the distillation. The compound shows no optical rotation.

***p*-Bromophenacyl Ester of Monocrotic Acid.**—This was prepared from monocrotic acid by the usual procedure. It was purified from aqueous ethanol: white needles, m. p. 78°.

Anal. Calcd. for $C_{15}H_{17}O_4Br$: C, 52.79; H, 5.02. Found: C, 53.0; H, 5.25.

B. Base Hydrochloride, $C_8H_{13}O_2N\cdot HCl$.—The aqueous solution obtained after ether extraction of the acid just described was evaporated *in vacuo* to dryness. The sirup thus obtained was dissolved in about 100 cc. of absolute ethanol, and the solvent removed by evaporation. A crystalline mass thus resulted which was extracted with three 30-cc. portions of boiling absolute ethanol to free from barium salts. The combined ethanolic extracts were concentrated to about 20 cc. and allowed to cool. The salt separated and the filtrate yielded an additional amount by addition of a little ether. It was recrystallized from absolute ethanol: white prisms, m. p. 161–162° (corr.); yield, 10.3 g. (87%).

Anal. Calcd. for $C_8H_{13}O_2N\cdot HCl$: C, 50.11; H, 7.36 Cl, 18.51. Found: C, 50.43; H, 7.22; Cl, 18.77.

Rotation. 1.20 g. made up to 25 cc. in ethanol at 25°. α_D −1.48; *l*, 2; $[\alpha]^{25}D$ −15.4°.

Retronecine Base.—A solution of the base hydrochloride in water was treated with one equivalent of *N* aqueous sodium hydroxide. It was then evaporated to dryness *in vacuo*. The oily residue was extracted with hot dry acetone, from which, after concentration and cooling, the crystalline base separated; purified from dry acetone: white irregular prisms, m. p. 121°. A mixed melting point with an authentic sample kindly furnished by Dr. R. H. F. Manske of the National Research Council of Canada, Ottawa, showed no depression.

Anal. Calcd. for $C_8H_{13}O_2N$: C, 61.91; H, 8.44. Found: C, 61.80; H, 8.46.

Rotation. 1.3316 g. made up to 25 cc. in ethanol at 28°. α_D +5.25; *l*, 2; $[\alpha]^{28}D$ +49.3°.

Diacetylretronecine Picrate.—The base was acetylated according to the directions of Barger[2b] for retronecine and the picrate formed by his procedure: yellow prisms, m. p. 146° (corr.).

Anal. (Dried at 100°.) Calcd. for $C_8H_{11}O_2N(OCCH_3)_2\cdot C_6H_3O_7N_3$: N, 11.95: Found: N, 11.5.

Hydrogenolysis of Monocrotaline

Monocrotalic Acid, $C_8H_{12}O_5$.—A solution of 10.8 g. of monocrotaline in a mixture of 10 cc. of glacial acetic acid and 40 cc. of ethanol was hydrogenated at 2–3 atm. with 0.1 g. of platinum oxide catalyst. In about five hours two moles of hydrogen had been absorbed and the reduction was complete. The solution was filtered from the catalyst and evaporated *in vacuo*. The remaining sirup was taken up in 34 cc. of *N* hydrochloric acid and the aqueous solution thus obtained extracted continuously with ether for twenty-four hours. The ether solution was dried over anhydrous sodium sulfate, the solvent removed *in vacuo*, and the crystalline acid thus obtained was purified by recrystallization from acetone–petroleum ether (b. p. 30–60°): white plates, m. p. 181–182° (corr.).

Anal. Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.43; neut. equiv., 188. Found: C, 51.06, 51.11; H, 6.43, 6.34; neut. equiv., 190.

Rotation. 1.1734 g. made up to 25 cc. in water at 28°. α_D −0.50; *l*, 2; $[\alpha]^{28}D$ −5.33.

If excess alkali is used in the determination of the neutral equivalent followed by back titration, values corresponding to between one and two carboxyls are obtained.

p-Bromophenacyl Ester of Monocrotalic Acid.—This was prepared by refluxing 0.68 g. of monocrotalic acid, exactly neutralized with alkali, with 1 g. of *p*-bromophenacyl bromide in 50% ethanol for five hours. The product was purified from ethanol: white crystals, m. p. 162–163° (corr.); yield, 0.47 g. (34%).

Anal. Calcd. for $C_{16}H_{17}O_6Br$: C, 49.87; H, 4.42. Found: C, 49.66; H, 4.46.

Rotation. 0.142 g. made up to 3.74 cc. in ethanol at 30.5°. α_D −1.07; *l*, 2; $[\alpha]^{30.5}D$ −14.1°.

Retronecanol, $C_8H_{15}ON$.—After extraction with ether of the acid just described, the aqueous solution was clarified with norite, filtered and made strongly alkaline with sodium hydroxide. It was then extracted with five 50-cc. portions of ether. The ether extracts were dried with anhydrous sodium carbonate and the ether removed *in vacuo*. The oily basic residue quickly solidified. It was best purified by distillation, 140° (30 mm.): white crystals, m. p. 95–96°.

Anal. Calcd. for $C_8H_{15}ON$: C, 68.04; H, 10.70; N, 9.91. Found: C, 67.90; H, 10.50; N, 10.09.

Rotation. 1.524 g. made up to 25 cc. in ethanol at 28°. α_D −11.0; *l*, 2; $[\alpha]^{28}D$ −91.1°.

Retronecanol Hydrochloride.—This product was prepared from retronecanol in the same manner as described for retronecine hydrochloride: white prisms from methanol–ether, m. p. 210° (corr.) with decomposition.

Anal. Calcd. for $C_8H_{15}ON\cdot HCl$: C, 54.03; H, 9.07. Found: C, 54.14; H, 9.14.

Retronecanol Methiodide.—This product was prepared by treating a dry ether solution of the base with the calculated amount of methyl iodide. It was purified from methanol–ether: white plates, m. p. 193° (corr.) with decomposition.

Anal. (Dried at 100°.) Calcd. for $C_8H_{15}ON\cdot CH_3I$: I, 44.88. Found: I, 45.22.

Rotation. 0.473 g. made up to 10 cc. in methanol at 27°. α_D −5.00; *l*, 2; $[\alpha]^{27}D$ −52.8.

Retronecanol Picrate.—The picrate was prepared in aqueous solution and was purified from water: thin yellow plates, m. p. 210° (corr.).

Anal. Calcd. for $C_8H_{15}ON\cdot C_6H_3O_7N_3$: N, 15.13. Found: N, 14.93.

Alkaline Degradation of Monocrotalic Acid to Monocrotic Acid.—A mixture of 5 g. of monocrotalic acid and 30 cc. of 10% aqueous sodium hydroxide was heated under reflux for one hour. The solution was then acidified and extracted rapidly with ether. After drying the ether solution over anhydrous sodium sulfate, the solvent was removed and the product distilled, b. p. 145–147° (20 mm.), d^{26}_4 1.072; $n^{19}D$ 1.4480.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.66; H, 8.39.

The acid gave a *p*-bromophenacyl ester, m. p. 78°, identical with that from monocrotic acid obtained directly from the monocrotaline.

Summary

The alkaloid, monocrotaline, is extracted by ethanol in good yields from *Crotalaria spectabilis* or *Crotalaria retusa*. It has the formula $C_{16}H_{23}O_6N$ and resembles the alkaloids occurring in various species of *Senecio*, *Heliotropium*, *Trichodesma* and *Erechtites*.

Monocrotaline undergoes alkaline hydrolysis to retronecine, $C_8H_{13}O_2N$, and an optically inactive, monobasic acid, $C_7H_{12}O_3$, called monocrotic acid. By hydrogenolysis monocrotaline gives retronecanol, $C_8H_{15}ON$, and an acid designated as monocrotalic acid, $C_8H_{12}O_5$.

It has been shown that monocrotalic acid is optically active, monobasic, and upon treatment with alkali gives the optically inactive acid, monocrotic acid, $C_7H_{12}O_3$, obtained by alkaline hydrolysis of the alkaloid.

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

Structure of Monocrotaline. II. Monocrotic Acid Obtained by Alkaline Hydrolysis of the Alkaloid[1]

BY ROGER ADAMS, E. F. ROGERS AND F. J. SPRULES[2]

By alkaline hydrolysis of monocrotaline, the alkaloid present in the seed of the *Crotalaria spectabilis* and *Crotolaria retusa*, there were obtained retronecine and an acid, $C_7H_{12}O_3$, called monocrotic acid.

$$C_{16}H_{23}O_6N + H_2O(BaO_2H_2) \longrightarrow \underset{\text{Retronecine}}{C_8H_{13}O_2N} + \underset{\text{Monocrotic acid}}{C_7H_{12}O_6} + [CO_2]$$

The same acid resulted when monocrotalic acid, $C_8H_{12}O_5$, obtained by hydrogenolysis of monocrotaline, was treated with aqueous alkali.

Monocrotic acid is optically inactive. It is monobasic and forms a monomethyl ester with diazomethane. The character of the third oxygen was determined by condensation of the methyl ester with dinitrophenylhydrazine. A hydrazone was formed in 85% yield and, since the ester shows no reducing action with Tollens' reagent or Feh-

(1) For previous paper see, Adams and Rogers, THIS JOURNAL, **61**, 2815 (1939).

(2) An abstract of a portion of a thesis submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.