distilled off under reduced pressure. The odor of benzaldehyde was detected in the distillate. The residual oil was distilled in vacuum; b.p. 140–150° (0.03 mm.); light yellow viscous oil, 4.90 g. (30%).

Anal. Calcd. for $C_{11}H_{13}BrO_3$: C, 48.31; H, 4.72. Found: C, 48.41; H, 4.72.

URBANA, ILLINOIS

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

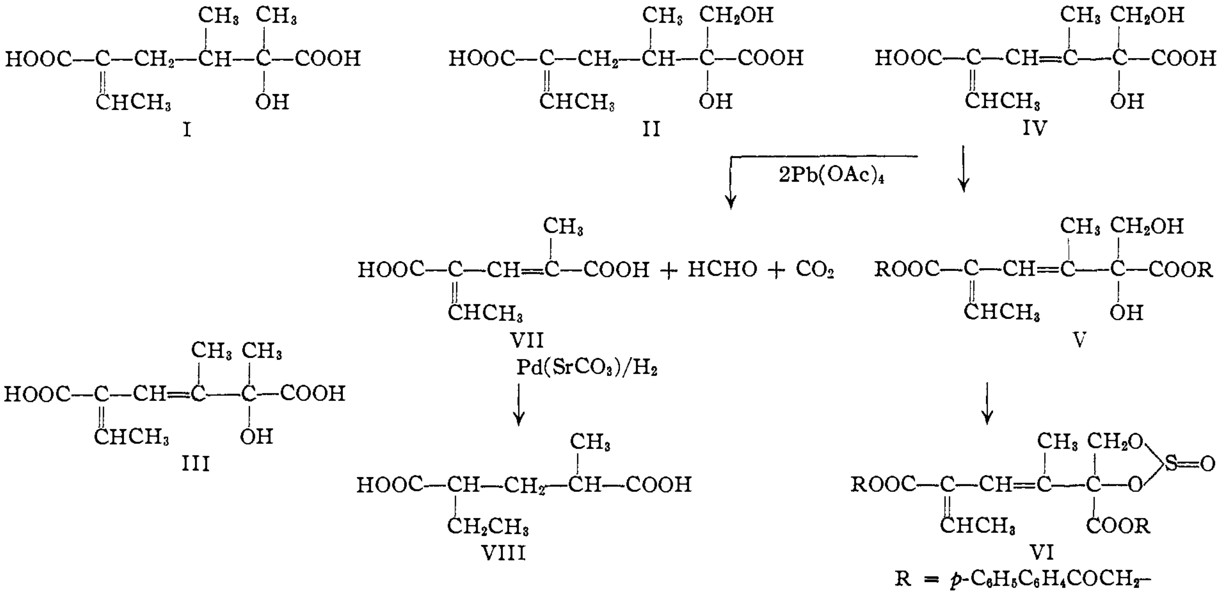
Riddelliine, the Alkaloid from *Senecio riddellii*. II. The Structure of Riddellic Acid and the Total Structure of Riddelliine

BY ROGER ADAMS AND BENJAMIN L. VAN DUUREN

RECEIVED MAY 7, 1953

Oxidation of riddellic acid, $C_{10}H_{14}O_6$, with two moles of lead tetraacetate afforded one mole of carbon dioxide, one mole of formaldehyde and a new crystalline, optically inactive, dibasic acid, $C_8H_{10}O_4$. Catalytic reduction of this acid gave *cis*-α-methyl-α′-ethylglutaric acid with the absorption of two moles of hydrogen. The presence of the glycol structure was confirmed by the preparation of a crystalline sulfite ester from bis-*p*-phenylphenacyl riddellate and thionyl chloride. A comparison of the infrared and ultraviolet absorption spectra of riddellic acid with that of α-longinecic acid, the structure of which has been determined in this Laboratory, indicated that the double bonds are similarly situated in the two acids. Riddellic acid is designated as 1,2-dihydroxy-3-methylhepta-3,5-diene-2,5-dicarboxylic acid. From the infrared absorption spectrum and oxidative degradation of dihydroriddelliine the total structure of riddelliine was determined.

In a previous communication from this Laboratory[1] a new alkaloid, riddelliine, from *Senecio riddellii* was described. It was shown that riddelliine, molecular formula $C_{18}H_{23}O_6N$, on aqueous alkaline hydrolysis afforded retronecine, the structure of which is known,[2] and a new dibasic acid, designated as riddellic acid. The presence of two double bonds in this acid was indicated by hydrogenation experiments. Further investigations on this acid are the subject of this report.



$HOOC{-}C({=}CHCH_3){-}CH_2{-}CH(CH_3){-}C(CH_3)(OH){-}COOH$ I

$HOOC{-}C({=}CHCH_3){-}CH_2{-}CH(CH_3){-}C(CH_2OH)(OH){-}COOH$ II

$HOOC{-}C({=}CHCH_3){-}CH{=}C(CH_3){-}C(CH_2OH)(OH){-}COOH$ IV

$\xrightarrow{2Pb(OAc)_4}$ $HOOC{-}C({=}CHCH_3){-}CH{=}C(CH_3){-}COOH + HCHO + CO_2$ VII

$\xrightarrow{Pd(SrCO_3)/H_2}$ $HOOC{-}CH(CH_2CH_3){-}CH_2{-}CH(CH_3){-}COOH$ VIII

$ROOC{-}C({=}CHCH_3){-}CH{=}C(CH_3){-}C(CH_2OH)(OH){-}COOR$ V

VI

$R = p\text{-}C_6H_5C_6H_4COCH_2{-}$

$HOOC{-}C({=}CHCH_3){-}CH{=}C(CH_3){-}C(CH_3)(OH){-}COOH$ III

Since the isolation of riddelliine and riddellic acid was described by Adams, *et al.*, the structure of a number of other C_{10} necic acids from Senecio alkaloids has been elucidated. Thus the structures of senecic acid[3] (I), retronecic and isatinecic (β-longinecic) acids[4,5] (II) and of α-longinecic acid (seneciphyllic acid)[6] (III), have now been completely elucidated. These acids all have the same carbon skeleton and differ only in the number of hydroxyl groups and carbon–carbon double bonds.

That these three acids and riddellic acid all have the same carbon skeleton was suggested earlier by Adams and Govindachari[7] who succeeded in separating and isolating the retronecine esters of senecic, isatinecic (β-longinecic), α-longinecic and riddellic acids from *Senecio longilobus*. Riddellic acid has now been shown to have structure IV.

Riddellic acid gave a strong coloration with ferric chloride, indicating the presence of an hy-

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[1] R. Adams, K. E. Hamlin, C. F. Jelinek and R. F. Philips, THIS JOURNAL, **64**, 2760 (1942).

[2] N. J. Leonard, "The Alkaloids" (Editors, R. H. F. Manske and H. L. Holmes), Vol. I, Academic Press, Inc., New York, 1950, p. 108.

[3] M. Kropman and F. L. Warren, *J. Chem. Soc.*, 2856 (1949); *ibid.*, 700 (1950).

[4] S. M. H. Christie, M. Kropman, E. C. Leisegang and F. L. Warren, *ibid.*, 1700 (1949).

[5] S. M. H. Christie, M. Kropman, L. Novellie and F. L. Warren, *ibid.*, 1703 (1949).

[6] R. Adams, T. R. Govindachari, J. H. Looker and J. D. Edwards, THIS JOURNAL, **74**, 700 (1952).

[7] R. Adams and T. R. Govindachari, *ibid.*, **71**, 1956 (1949); **71**, 1180 (1949).

TABLE I

INFRARED ABSORPTION FREQUENCIES

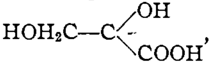
	C═C	RR'>C═CHR	Ester carbonyl	Acid carbonyl	Hydroxyl stretching	S═O
Riddelliine[a]	1640 1660		1715 1737		3580	
α-Longilobine[a,c]	1645 1664		1717 1740			
Riddellic acid[a]	1637	825 850		1675 1695 1720	3350 3452	
α-Longinecic acid[a,c]	1640	825 850		1680 1700 1730	3440	
Dimethyl riddellate[b,g]	1650	830 860	1725		3500	
Dimethyl α-longinecate[b,h]	1650	830 860	1725		3500	
Dihydroriddelliine[a,d]	1655	820 855	1707		3400 3500 3600	
α-Methyl-α'-ethylidineglutaconic acid[a]	1630	815 850		1682		
Bis-*p*-phenylphenacyl riddellate sulfite[a,e]	1658		1720 1748			1200–1250
Riddelliine sulfite hydrochloride[a,f]	1665		1720 1740			1210 1230 1240

[a] Nujol mull. [b] Pure liquids. [c] Ref. 7. [d] Band for carboxylate ion at 1635 cm.$^{-1}$ and salt structure band at 2200–2500 cm.$^{-1}$. [e] Conjugated keto carbonyl band at 1705 cm.$^{-1}$. [f] Salt structure band at 2250 cm.$^{-1}$. [g] Prepared by previously described method, ref. 1. [h] Prepared by previously described method, ref. 6.

droxyl α to a carboxyl.[8] A positive reaction with fuchsin in Criegee's test[9] indicated the presence of a glycol.

The bis-*p*-phenylphenacyl ester of riddellic acid (V), which was obtained as a crystalline solid, reacted readily with thionyl chloride at 0°. The resultant crystalline product analyzed correctly for the sulfite ester of bis-*p*-phenylphenacyl riddellate (VI). The infrared absorption spectrum of this compound showed a band in the sulfur-oxygen double bond region, typical of sulfite esters derived from vicinal glycols.[10] The infrared absorption spectrum of the sulfite ester of riddelline, which also was prepared, showed the same characteristic band (see Table I).

Riddellic acid was readily oxidized with lead tetraacetate in aqueous solution, two moles of oxidizing agent being required to complete the oxidation. In a quantitative study of the oxidation, one mole of carbon dioxide and one mole of formaldehyde, isolated as its dimedone derivative, were obtained per mole of acid oxidized. From the aqueous solution, after removal of the lead as sulfate, a new crystalline acid (VII) was obtained. This acid, $C_8H_{10}O_4$, was dibasic and optically inactive. The infrared absorption spectrum showed a single band at 1682 cm.$^{-1}$ indicating only conjugated acid carboxyl and a conjugated C═C band at 1630 cm.$^{-1}$. On hydrogenation with a palladium–strontium carbonate catalyst two moles of hydrogen was smoothly and stereospecifically absorbed and a crystalline acid obtained. This acid, m.p. 70°, was shown to be identical with *cis*-α-methyl-α'-ethylglutaric acid (VIII) synthesized by the method of Rydon.[11] A mixture of the two acids gave no depression of melting point on admixture and their infrared absorption spectra were identical.

The presence in riddellic acid of the grouping  $\mathrm{HOH_2C{-}C}\left<\begin{matrix}\mathrm{OH}\\ \mathrm{COOH}\end{matrix}\right.$, as found in isatinecic and retronecic acids, and the presence of the α-methyl-α'-ethylglutaric acid skeleton as in all the C_{10} necic acids mentioned above, have thus been established.

The structure of α-longinecic acid has been carefully studied by Adams, *et al.*[6] Ozonization experiments and infrared absorption spectra indicated the absence of terminal methylene groups. A comparative study of the infrared absorption spectra of riddelliine and α-longilobine, riddellic and α-longinecic acids and of their dimethyl esters therefore seemed desirable. The important absorption frequencies are summarized in Table I. The alkaloids show two bands in the ester carbonyl region, one corresponding to an unconjugated ester and the other to a conjugated ester. Two bands in the C═C region of both alkaloids correspond to conjugated and unconjugated carbon-carbon double bonds. The only differences in the absorption spectra of the alkaloids are in the hydroxyl stretching region. α-Longilobine shows no absorption in this region whereas riddelliine shows a band at 3580 cm.$^{-1}$. A similar band occurs in the closely related β-longilobine[7] at 3585 cm.$^{-1}$, which like riddelliine has two vicinal alcoholic hydroxyls.

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[8] A. Berg, *Bull. soc. chim.*, **11**, 882 (1894).

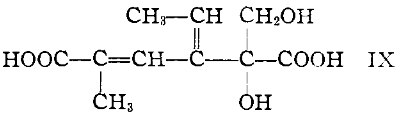
[9] R. Criegee, *Ber.*, **64**, 260 (1931).

[10] R. Adams, P. R. Shafer and B. H. Braun, THIS JOURNAL, **74**, 5612 (1952); J. Cymerman and J. B. Willis, *J. Chem. Soc.*, 1332 (1951).

[11] H. N. Rydon, *J. Chem. Soc.*, 1944 (1936).

Riddellic and α-longinecic acids and their dimethyl esters show one band in the C=C region. The acids and their dimethyl esters showed bands at 825 and 855 cm.$^{-1}$ which may be ascribed to the structure $RR'C{=}CHR$.[6] In addition, α-longinecic and riddellic acids show three bands in the acid carbonyl region, the band at 1680 and 1675 cm.$^{-1}$, respectively, corresponding to the conjugated acid carbonyl. The other two bands may be attributed to the unconjugated acid carbonyl.[12] The infrared absorption spectra of the acids differ in the hydroxyl stretching region. α-Longinecic acid has only one band in this region whereas riddellic acid has two bands. β-Longinecic acid[7] (II), like riddellic acid, has two bands in this region, *viz.*, at 3350 and 3525 cm.$^{-1}$.

The close similarity of the infrared absorption spectra of α-longinecic acid, riddellic acid and of their retronecine and dimethyl esters indicates that the double bonds in these two acids are similarly situated. This leaves only two possible structures for riddellic acid, IV and IX.



$$\mathrm{HOOC{-}\underset{\displaystyle CH_3}{C}{=}CH{-}\overset{\displaystyle CH_3{-}CH}{\overset{\|}{C}}{-}\overset{\displaystyle CH_2OH}{\underset{\displaystyle OH}{C}}{-}COOH}$$

IX

Compound IV is the more likely on the basis of its possible formation from two isoprene units.

The ultraviolet absorption spectra of α-longinecic and riddellic acids were next compared, Table II.

TABLE II

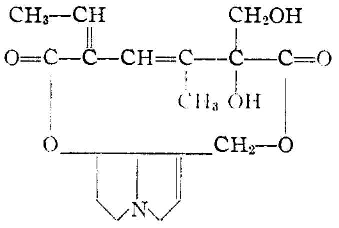
ULTRAVIOLET ABSORPTION SPECTRA: SOLVENT 95% ETHANOL

	λmax, mμ	εmax
Riddellic acid	215	8300
α-Longinecic acid	214	8450
	214[6]	8130[6]

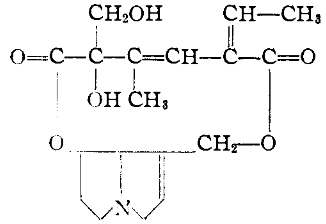
Adams, *et al.*,[6] noted that the ultraviolet absorption spectrum of α-longinecic acid is characteristic of an α,β-unsaturated acid. The possibility of a 1,3-diene system in complete conjugation with a carboxyl group in α-longinecic acid, as in sorbic acid, was excluded on the basis of previously published results.[13] In view of the close similarity between the ultraviolet absorption spectra of α-longinecic and riddellic acids it may be concluded that the double bonds are similarly placed in the two acids and that no 1,3-diene system in complete conjugation with a carboxyl is existent in riddellic acid. This would exclude structure IX and leave structure IV as the only structure for riddellic acid which accounts for the chemical and spectral evidence.

With the structure of riddellic acid now elucidated, two possible structures for the alkaloid may be written (X and XI).

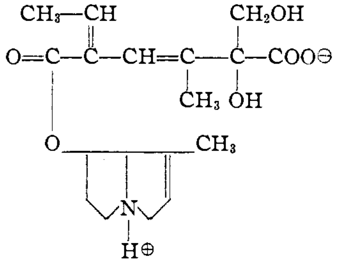
In order to decide between these two structures riddelliine was hydrogenated with a palladium–strontium carbonate catalyst. One mole of hydrogen was absorbed. The resulting crystalline product exhibited the properties of an amino acid (XII). The infrared absorption spectrum of this compound showed the typical salt structure band at 2200–2500 cm.$^{-1}$, a band corresponding to a conjugated ester carbonyl at 1707 cm.$^{-1}$ and a band characteristic of the carboxylate ion at 1635 cm.$^{-1}$. It is therefore clear that during the hydrogenation the allyl ester was cleaved and since X and not XI would give a conjugated ester after cleavage, it follows that riddelliine has structure X and dihydroriddelliine structure XII.



X

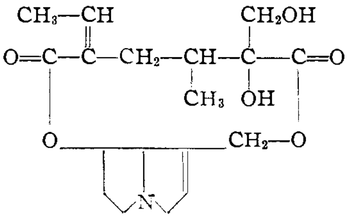


XI



XII

Additional support for structures X and XII was obtained by the lead tetraacetate oxidation of dihydroriddelliine. One mole of carbon dioxide was liberated which indicated the presence of an α-hydroxy acid. Structure XI would not give an α-hydroxy acid on reduction. During a control experiment riddelliine was treated with lead tetraacetate under the same conditions used in the oxidation of dihydroriddelliine. No carbon dioxide was evolved. Leisegang and Warren[14] assigned to isatidine the structure XIII. These workers reduced isatidine to an *oily* reduction product which gave on oxidation with lead tetraacetate one mole of carbon dioxide.



XIII

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[12] In malonic acid there are two bands in the acid carbonyl region, *viz.*, at 1742 and 1705 cm.$^{-1}$ corresponding to the monomer and dimer, respectively.

[13] E. A. Braude, *Ann. Repts. Progress Chem.* (*Chem. Soc., London*), **42**, 114 (1945).

[14] E. C. Leisegang and F. L. Warren, *J. Chem. Soc.*, 702 (1950).

It should be noted that in attempting to use the method described by Leisegang and Warren[14] for the quantitative determination of carbon dioxide reliable results could not be obtained. These workers oxidized hydrogenated isatidine with lead tetraacetate in glacial acetic acid which had been saturated with carbon dioxide at room temperature. Control experiments conducted by us indicated that when one gram of lead tetraacetate was added to 10 ml. of glacial acetic acid (the same quantities used by Leisegang and Warren) saturated with carbon dioxide at room temperature, 12.0 ml. (S.T.P.) of carbon dioxide was liberated.[14a] In this investigation dihydroriddelliine was oxidized with lead tetraacetate in aqueous solution.

Acknowledgment.—The authors are indebted to Mr. J. Nemeth, Mrs. Esther Fett and Mrs. L. Chang for the microanalyses, Miss Helen Miklas for the infrared absorption spectra and to Miss Barbara Burnett for the ultraviolet absorption spectra.

Experimental[15]

All melting points are corrected.

Riddellic Acid.—Riddelliine was hydrolyzed with aqueous barium hydroxide as described in Part I of this series. The anhydrous acid crystallized with difficulty from dry ether–benzene at room temperature; prisms, m.p. 101–102° (lit.[1] m.p. 102–103°).

Lead Tetraacetate Oxidation of Riddellic Acid. (a) α-Methyl-α′-ethylidineglutaconic Acid.—A solution of 3.90 g. of riddellic acid in 60 ml. of water was heated on a steam-cone and 16.5 g. of lead tetraacetate added in small portions at a time over one hour. During the addition of lead tetraacetate a brown precipitate separated, gas bubbles were evolved and the odor of formaldehyde was detected. After the addition of oxidizing agent was complete, the solution was heated for an additional half-hour on the steam-cone. The clear, light-yellow solution was cooled in ice and 100 ml. of 30% sulfuric acid added. The solution was allowed to stand in ice for one hour. The precipitated lead sulfate was filtered off and the filtrate extracted with ether. The ether extract was washed with water, dried over anhydrous magnesium sulfate and filtered. Removal of the solvent left 2.2 g. (76%) of a colorless oil. On standing in a vacuum desiccator the oil crystallized. The product was purified by vacuum sublimation at 100° and 0.5 mm.; m.p. 114°.

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.47; H, 5.88. Found: C, 56.46; H, 5.98.

(b) **Quantitative Determination of Carbon Dioxide.**—A solution of 0.460 g. of anhydrous riddellic acid in 5 ml. of boiled-out distilled water was treated with 2.0 g. of lead tetraacetate. The mixture was heated at 100° for one hour and the carbon dioxide evolved collected in a gas buret over a saturated solution of sodium chloride which had also been saturated with carbon dioxide at room temperature.

Calcd. for one mole from $C_{10}H_{14}O_6$: 44.80 ml. at S.T.P. Found: 39.10 ml. at S.T.P.

(c) **Formaldehyde.**—A solution of 0.617 g. of anhydrous riddellic acid in 5 ml. of water was treated with 2.10 g. of lead tetraacetate. The mixture was heated at 100° for one hour and the liberated formaldehyde steam distilled into a saturated aqueous solution of 1 g. of dimedone. A crystalline product separated; m.p. 189–190°; 0.40 g. (52%). The melting point was undepressed on admixture with an authentic sample of formaldehyde–dimedone, m.p. 189–190°. The solutions left after determinations (b) and (c) above, both yielded α-methyl-α′-ethylidineglutaconic acid as described under (a) above.

***cis*-α-Methyl-α′-ethylglutaric Acid.**—Ethyl α-bromoisobutyrate and diethyl ethylmalonate were condensed by the previously described method of Rydon[11] and the product hydrolyzed and decarboxylated. *cis*-α-Methyl-α′-ethylglutaric acid was obtained by conversion of the mixture of diastereoisomeric acids to the imides followed by separation and hydrolysis. The acid was purified by crystallization from a hydrochloric acid–water (1:1) mixture; prisms, m.p. 70–71° (lit.[11] m.p. 63°).

Catalytic Reduction of α-Methyl-α′-ethylidineglutaconic Acid.—A solution of 70 mg. of the unsaturated acid in 10 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure in presence of 20 mg. of palladium–strontium carbonate (6%) catalyst. Two moles of hydrogen was rapidly absorbed. The catalyst was filtered off and the filtrate taken to dryness under reduced pressure. The resultant oil, 62 mg., crystallized on standing, m.p. 50–55°. After two recrystallizations from a hydrochloric acid–water (1:1) mixture the acid melted at 70–71°. On admixture with *cis*-α-methyl-α′-ethylglutaric acid, there was no depression of melting point. The infrared absorption spectra of these two preparations were identical.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.17; H, 8.04. Found: C, 55.09; H, 8.19.

Bis-*p*-phenylphenacyl Riddellate.—This ester was prepared from equivalent amounts of the sodium salt of the acid and *p*-phenylphenacyl bromide by the usual procedure. The resultant oil crystallized from ethanol-water and was purified by recrystallization from the same solvent; m.p. 59–60°.

Anal. Calcd. for $C_{38}H_{34}O_8$: C, 73.78; H, 5.50. Found: C, 73.81; H, 5.60.

Rotation.—6.0 mg. made up to 1.60 ml. with 95% ethanol at 28° gave α_D −0.142°; l 1, $[\alpha]^{28}_D$ −38.3° (±1.0°).

Bis-*p*-phenylphenacyl Riddellate Sulfite.—To 3 ml. of thionyl chloride at 5° 0.5 g. of bis-*p*-phenylphenacyl riddellate was added and the mixture allowed to heat to room temperature. The excess thionyl chloride was removed at 25° under reduced pressure, the oily residue washed with benzene and crystallized from 95% ethanol; nodules, m.p. 78–80° (dec.).

Anal. Calcd. for $C_{38}H_{32}O_9S$: C, 68.67; H, 4.81. Found: C, 68.52; H, 5.08.

Rotation.—6.0 mg. made up to 1.60 ml. with 95% ethanol at 28° gave α_D −0.042°; l 1, $[\alpha]^{28}_D$ −11.3° (±1.0°).

Riddelliine Sulfite Hydrochloride.—This compound was prepared by the method previously used for the preparation of monocrotaline sulfite hydrochloride.[10] One gram of riddelliine was added slowly to 5 ml. of thionyl chloride at 5° and the mixture allowed to heat to room temperature. Removal of the excess reagent under reduced pressure left a crystalline residue, which was washed with benzene, 1.20 g. (99%). The product was recrystallized from 95% ethanol, m.p. 215° (dec.).

Anal. Calcd. for $C_{18}H_{21}O_7NS \cdot HCl$: C, 50.11; H, 5.10; N, 3.24. Found: C, 49.98; H, 5.26; N, 3.09.

Rotation.—11.0 mg. made up to 1.60 ml. with 95% ethanol at 28° gave α_D −0.282°; l 1, $[\alpha]^{28}_D$ −41.5° (±1.0°).

Riddelliine Sulfite,—A solution of 1 g. of riddelliine sulfite hydrochloride in 20 ml. of water was cooled to 5° and a cold solution of 1.0 g. of sodium bicarbonate in 10 ml. of water added. On swirling the whole solution set to a white gelatinous mass. The base was extracted by stirring with chloroform. The aqueous solution was extracted twice more with chloroform and the combined chloroform solutions washed, first with cold dilute sodium bicarbonate and then with water. The extract was dried over anhydrous magnesium sulfate and the chloroform removed under reduced pressure. A crystalline residue 0.80 g. (88%) was left. The product was recrystallized from 95% ethanol; needles, m.p. 170° (dec.).

Anal. Calcd. for $C_{18}H_{21}O_7NS$: C, 54.68; H, 5.31; N, 3.54. Found: C, 54.34; H, 5.46; N, 3.57.

Rotation.—21.4 mg. made up to 1.60 ml. with chloroform at 28° gave α_D −0.232°; l 1, $[\alpha]^{28}_D$ −17.4° (±1.0°).

Dihydroriddelliine.—A solution of 3 g. of riddelliine in 150 ml. of 95% ethanol was shaken with hydrogen at 3 to 4

[14a] Since this paper was submitted for publication L. J. Dry and F. L. Warren [*J. S. African Chem. Inst.*, **6**, 14 (1953)] reported that when using this method a blank correction of 9.0 ml. had to be applied when 10 ml. of glacial acetic acid (saturated with carbon dioxide at room temperature) and one gram of lead tetraacetate were used in the reaction. This blank correction was not mentioned in the original report of the method by Liesegang and Warren.

[15] The riddelliine used in this investigation was extracted from *Senecio riddellii* by P. R. Shafer in this Laboratory. Also, dihydroriddelliine and riddelliine sulfite hydrochloride were first prepared by him.

atmospheres in presence of one gram of palladium–strontium carbonate catalyst (6%). After 3 hours one mole of hydrogen was absorbed. The catalyst was filtered off, washed with warm ethanol and the filtrate taken to dryness under reduced pressure. The residue was crystallized from 95% ethanol. The product, 1.0 g. (33%), was recrystallized from the same solvent; prisms, m.p. 197°. The mother liquors from the crystallization of the crude product left on evaporation an oil which resisted crystallization.

Anal. Calcd. for $C_{18}H_{25}O_6N$: C, 61.53; H, 7.12; N, 3.99. Found: C, 61.97; H, 6.85; N, 3.95.

Rotation.—9.0 mg. made up to 1.60 ml. with water at 28° gave α_D +0.125°; l 1, $[\alpha]^{28}_D$ +22.3° (±1.0°).

Lead Tetraacetate Oxidation of Dihydroriddelliine; Determination of Carbon Dioxide.—A solution of 0.40 g. of dihydroriddelliine in 10 ml. of water saturated with sodium chloride was treated with 1.0 g. of lead tetraacetate. After a short induction period carbon dioxide was steadily evolved and collected in a gas buret as described above. After 30 minutes no more gas was evolved. The reaction vessel was heated for 5 minutes at 60° and allowed to cool to room temperature.

Calcd. for one mole of CO_2 from $C_{18}H_{22}O_6N$: 25.6 ml. at S.T.P. Found: 19.00 ml. at S.T.P.

URBANA, ILLINOIS

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

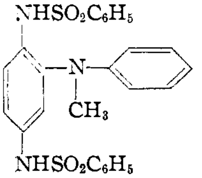
Quinone Imides. XXX. Addition of Primary and Secondary Aromatic Amines

BY ROGER ADAMS, B. H. BRAUN AND SEYMOUR H. POMERANTZ

RECEIVED MAY 9, 1953

Methylaniline, dimethylaniline and diethylaniline add to *p*-quinonedibenzenesulfonimide and its 2-methyl derivatives differently from aniline, ring substituted anilines or aliphatic and alicyclic amines. They add 1,4 by the proton in the *p*-position to the amino groups reacting with one of the benzenesulfonimide nitrogens and the aminophenyl residue entering the quinone imide ring, thus resulting in biphenyl derivatives. The methylaniline adduct was converted to the dimethylaniline adduct by methylation. Aromatic primary and secondary amines add to 1,4-naphthoquinonedibenzenesulfonimide, however, by separation of the proton from the nitrogen atom; dimethylaniline merely causes reduction to the diamide.

In the study of the reactions of amines with *p*-quinonedibenzenesulfonimide,[1] it was noted that monomethylaniline reacted differently from the other secondary amines and aniline. No succession of reactions occurred and the product in good yield was an adduct of the amine to the quinone diimide in mole to mole ratio. The structure assigned to it is shown in I and was originally accepted on the basis of analogy to the initial product obtained by the addition of morpholine to the diimide.[1]



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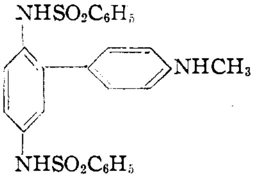
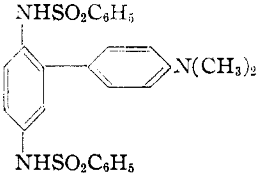


II



III

Aniline and dimethylaniline add to tetrachloro-*p*-quinonedibenzenesulfonimide[2] in an unexpected fashion. A 1,6-addition to the two imide nitrogens occurs with the proton from the position para to the amino or dimethylamino group attacking one imide nitrogen and the aminophenyl residue the other. The difference in properties of the methylaniline from the other amine adducts with the unsubstituted quinone diimide and the character of the products of the aromatic amines with the tetrachloro diimide suggested a restudy of the methylaniline and *p*-quinonedibenzenesulfonimide adduct to determine whether it might not have structure II.

The methylaniline adduct (I or II) was methylated with excess methyl iodide in dimethylformamide as solvent. One methyl group was introduced. The infrared absorption spectrum of the methylated product showed marked similarities to that of the product from which it was formed. The methylaniline adduct has two N–H bands, one of medium intensity at 3178 cm.$^{-1}$ and one weak at 3386 cm.$^{-1}$; the methylated product has a single band of medium intensity at 3184 cm.$^{-1}$.

The addition of dimethylaniline to *p*-quinonedibenzenesulfonimide was next attempted. The reaction proceeded smoothly and the resulting product (III) was found to be identical with the methylated methylaniline adduct by infrared spectra and by a melting point of the mixture of the two. This not only established the constitution of the dimethylaniline adduct, but also confirmed the structure of the monomethylaniline derivative as II. Diethylaniline was found to add in similar fashion.

Dimethylaniline was added successfully to 2-methyl-1,4-benzoquinonedibenzenesulfonimide with the formation of a product in 75% yield which was formulated as IV, with the dimethylaniline group in the 5-position by analogy to the addition of other molecules to 2-methyl-*p*-quinonedibenzenesulfonimide.

The addition of aniline and morpholine in glacial acetic acid to 1,4-naphthoquinonedibenzenesulfonimide has been previously described.[3] The complicated reactions occurring in the corresponding benzene series[1] were not encountered, and the addition of one mole of amine to one mole of diimide resulted. The aniline derivative was assigned the structure V. When monomethyl-

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[1] R. Adams and K. A. Schowalter, THIS JOURNAL, **74**, 2597 (1952).

[2] R. Adams and B. H. Braun, *ibid.*, **74**, 5869 (1952).

[3] R. Adams and R. A. Wankel, *ibid.*, **73**, 131 (1951).