melts at 179–180°, it is obvious that these authors did not have the product reported.

4-Benzenesulfonamido-2-chloro-1-naphthol.—(C) A solution of 1.5 g. of 4-nitro-2-chloro-1-naphthol in 15 ml. of methanol was treated with 0.1 g. of platinum oxide and shaken with hydrogen at 40 p.s.i. for 2 hours. After filtration, 50 ml. of dry ether was added and the solution was saturated with dry hydrogen chloride. A gray hydrochloride salt separated. This was dissolved in 5 ml. of methanol and precipitated by the slow addition of 50 ml. of dry ether. Treatment of the white hydrochloride in 10 ml. of pyridine with 0.9 g. of benzenesulfonyl chloride caused evolution of considerable heat and a dark coloration developed. The solution was poured into 50 ml. of dilute hydrochloric acid, stirred well and filtered. The dark brown precipitate was recrystallized twice from 88% formic acid (Darco), then three times from 88% formic acid alone, to yield a white product, m. p. 187–188° (cor.). The yield was 0.2 g. (9%).

3-Chloro-1,4-naphthoquinone 1-Benzenesulfonimide.—4-Benzenesulfonamido-2-chloro-1-naphthol was oxidized by gently warming and stirring in a minimum amount of glacial acetic acid with one molecular equivalent of lead tetraacetate. After thorough cooling, the yellow product was collected on a filter and recrystallized from glacial acetic acid; yellow needles, m. p. 180–181° (cor.). The yields varied from 45 to 75%.

Anal. Calcd. for $C_{16}H_{10}ClNO_3S$: C, 57.92; H, 3.04; N, 4.22. Found: C, 57.86; H, 3.11; N, 4.48.

Reaction of 1,4-Naphthoquinone Dibenzenesulfonimide with Sodium Hydroxide.—A suspension of 0.5 g. of 1,4-naphthoquinone dibenzenesulfonimide in 10 ml. of 5% sodium hydroxide was heated with vigorous stirring for one hour. Most of the naphthoquinone diimide went into solution, giving a dark coloration. After neutralization with acetic acid, the brown precipitate was collected on a filter. Recrystallization from glacial acetic acid gave 0.37 g. of naphthylene-1,4-dibenzenesulfonamide, m. p. 250–251° (cor.).

Summary

1. The dibenzenesulfonimido, dimethanesulfonimido and di-*p*-toluenesulfonimido derivatives of 1,4-naphthoquinone have been prepared from the corresponding diamides by oxidation with lead tetraacetate.

2. These compounds add in glacial acetic acid as solvent hydrogen chloride, aniline, morpholine and thiophenol with formation in excellent yield of the corresponding 2-substituted naphthalene-1,4-disulfonamides. These adducts, with the exception of the anilino compound, were oxidized to the substituted 1,4-naphthoquinone diimides. The 1,4-naphthoquinone disulfonimides are stable under ordinary conditions.

3. The 2-chloro-1,4-naphthoquinone dibenzenesulfonimide adds hydrogen chloride to give 2,3-dichloronaphthalene-1,4-dibenzenesulfonamide. Thiophenol, however, does not add but is merely oxidized with resulting reduction of the quinone diimide. 2-Phenylmercapto-1,4-naphthoquinone dibenzenesulfonimide similarly adds hydrogen chloride and is reduced by thiophenol.

4. 1,4-Naphthoquinone dibenzenesulfonimide is reduced to the corresponding dibenzenesulfonamide by means of platinum and hydrogen. It is also reduced slowly to the diamide by boiling with dilute aqueous sodium hydroxide. Upon boiling with concentrated hydrochloric acid in glacial acetic acid, partial hydrolysis occurs, followed by addition of hydrogen chloride. The structure of the resulting product, 4-benzenesulfonamido-2-chloro-1-naphthol, was proved through synthesis by an unequivocal method.

URBANA, ILLINOIS RECEIVED JULY 12, 1950

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

The Identity of α-Longilobine and Seneciphylline

BY ROGER ADAMS AND JAMES H. LOOKER

The difficulty of purification of many *Senecio* alkaloids has frequently been encountered by investigators in this field, and the presence usually of more than one closely related alkaloid in a single plant has been established. Minute quantities of impurities of related substances modify markedly the optical rotation and melting points of the products. The identification and separation of four alkaloids from *Senecio longilobus* and two or more of the same alkaloids from several other *Senecio* species have been achieved.[1] These results are indicative that certain *Senecio* alkaloids already described may be mixtures of one or more of these same four but have not been immediately recognized from the reported constants. Warren, *et al.*,[2] have established the identity of retrorsine with β-longilobine.

A comparison has now been made of seneciphylline and α-longilobine. Seneciphylline was first isolated by Orekhov and Tiedebel, from *Senecio platyphyllus*,[3] and later from *Senecio stenocephalus*.[4] Manske has shown this alkaloid to be the principal base occurring in *Senecio spartioides*.[5] Quite recently a structural study of seneciphylline[6] has shown that the hydrolysis products of this alkaloid, $C_{18}H_{23}O_5N$, are retronecine, the structure of which is well established,[7] and a dibasic acid of molecular formula $C_{10}H_{14}O_5$. The melting point of the acid depends upon the mode of hydrolysis; aqueous alkali results in isoseneciphyllic acid, m. p. 105–108°, whereas ethanolic potassium hydroxide gives seneciphyllic acid, m. p. 144–145°. The possibility of *cis–trans* isomerism has been postulated to account for the isomeric acids, and the conversion of isoseneciphyllic acid to seneciphyllic acid under the influence of hydrochloric acid supports this theory. Seneciphylline is thus an ester, in which in all probability the two hydroxyl groups of retronecine are esterified by the two carboxyl groups of isoseneciphyllic acid. Recent work by Warren and co-workers indicates that the action of aqueous potassium hydroxide parallels that of barium hydroxide in the hy-

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(1) Adams and Govindachari, THIS JOURNAL, **71**, 1956 (1949).

(2) Warren, Kropman, Adams, Govindachari and Looker, *ibid.*, **72**, 1421 (1950).

(3) Orekhov and Tiedebel, *Ber.*, **68**, 650 (1935).

(4) Konovalova and Orekhov, *Bull. soc. chim.*, [5] **4**, 2037 (1937).

(5) Manske, *Can. J. Research*, **B17**, 1 (1939).

(6) Konovalova and Danilova, *Zhur. Obshchei Khim.*, **18**, 1198 (1948).

(7) Adams and Leonard, THIS JOURNAL, **66**, 257 (1944).

TABLE I

Alkaloid	M. p., dec. °C.,[a]	$[\alpha]_D$ $CHCl_3$	Methiodide m. p. (dec.) °C.	Aurichloride, m. p. (dec.) °C.	Picrate, m. p., °C.	Reference
Seneciphylline	217–218	−128.04	231–232	162–163	182–183	Orekhov[3]
	217	−119.5	.....	.....	189[b]	Manske[5]
	216[c]	−120.6	241	161–163	188–189	Present work
α-Longilobine	217–218	−125.2	240	.....	....	Adams and Govindachari[9]
	217[d]	.....	240	162–164	187–188.5	Present work
Equimolar mixture	216[e]	.....	240	161–163	187–189	Present work

[a] All melting points except those of Orekhov,[3] are corrected. [b] Obtained by Konovalova[4] from material isolated by Manske. [c] Obtained by recrystallizing the alkaloid, $[\alpha]_D$ −120.6°, once from absolute ethanol. [d] Observed when α-longilobine, $[\alpha]_D$ −125.2°, was recrystallized once from absolute ethanol. [e] All melting points were taken simultaneously in the same bath with the corresponding derivatives of seneciphylline and α-longilobine.

drolysis of *Senecio* alkaloids of this type, but that ethanolic potassium hydroxide isomerizes the *cis* form of a necic acid to the more stable *trans* isomer.[8]

By the use of chromatographic techniques, Adams and Govindachari isolated α-longilobine, β-longilobine, senecionine and riddelliine from the total alkaloid of *Senecio longilobus*.[1,9] α-Longilobine was shown to have an empirical formula $C_{18}H_{23}O_5N$, identical with that of seneciphylline, and upon hydrolysis gave retronecine[7] and the dibasic α-longinecic acid, m. p. 114–115°, of molecular formula $C_{10}H_{14}O_5$, identical with that of isoseneciphyllic or seneciphyllic acid.

A generous sample of seneciphylline was provided us by Dr. Manske for our work. The methiodides, aurichlorides and picrates were prepared from this product and carefully purified. These were compared with the same derivatives of α-longilobine purified with equal care by the same procedures. The results are shown in Table I. These values establish the identity of the two alkaloids and the identity was confirmed unequivocally by infrared spectra[9] of the bases.

It is evident that α-longinecic acid and isoseneciphyllic acid must also be identical. However, since a considerable discrepancy existed between the melting point of α-longinecic acid and that reported for isoseneciphyllic acid, the hydrolysis of seneciphylline and α-longilobine under identical conditions has been effected. α-Longinecic acid, m. p. 111–113° (cor.) and isoseneciphyllic acid, m. p. 110–111° (cor.) have been obtained; these values are in reasonable agreement with that of 114–115° (cor.) reported for α-longinecic acid by Adams and Govindachari.[9] The melting point of the mixture shows no depression. The dependence of the melting points of certain necic acids upon the rate of heating has been previously noted.[2] Comparison of the infrared absorption spectrum of isoseneciphyllic acid with the published spectrum of α-longinecic acid[9] confirmed the identity of the two acids.

The presence of the same carbon skeleton in the acid moieties of α-longilobine, β-longilobine, senecionine and riddelliine was postulated as very probable in a previous paper from this Laboratory.[1] Since then Warren, *et al.*,[8,10,11] have confirmed this suggestion in part by establishing that the two pairs of geometric isomers, the first isatinecic (β-longinecic) and retronecic acids and the second integerrinecic and senecic acids have the same skeleton. They now reiterate our point of view and extend it to include all necic acids.

We acknowledge the preliminary study and suggestions of Mr. Bernard H. Braun. We are indebted to Miss Elizabeth Petersen for the infrared spectra determinations.

Experimental

Melting Point Determinations.—Melting points of the alkaloids were obtained by inserting the capillary tube in an oil-bath at room temperature, heating rapidly to 180°, then at a rate of 5° per minute. All decomposition melting points recorded are the temperatures at which the compound was just completely melted. Derivative melting points were taken by heating fairly rapidly from room temperature to within 10° of the melting point, then at a rate of 2° per minute.

α-Longilobine and Seneciphylline Picrates.—To a solution of 22 mg. of picric acid in absolute ethanol was added a hot, absolute ethanolic solution of 32 mg. of α-longilobine. The bright yellow picrate resulting was removed by filtration and recrystallized from absolute ethanol. Seneciphylline picrate was prepared by the same procedure.

α-Longilobine and Seneciphylline Aurichlorides.—The yellow aurichlorides crystallized upon adding a few drops of concentrated aqueous gold chloride to a solution of 50 mg. of the alkaloid in 1 *N* HCl. Recrystallization was effected by suspending the crude derivative in 3 *N* HCl, heating, adding just enough absolute ethanol to give complete solution, and permitting the resulting solution to evaporate slowly overnight.

α-Longilobine and Seneciphylline Methiodides.—The methiodides were obtained by treating 50 mg. of the alkaloid in 6–7 ml. of boiling chloroform with a large excess of methyl iodide. The colorless methiodide crystallized upon cooling and was collected by filtration. Recrystallization was effected by suspending the derivative in hot absolute ethanol, adding just enough water to give complete solution and permitting the mixture to evaporate slowly overnight.

Hydrolysis of α-Longilobine and Seneciphylline by Aqueous Barium Hydroxide.—The procedure employed is a modification of the ones used by Adams and Govindachari[9] and by Warren and co-workers.[8]

To a suspension of 500 mg. of α-longilobine in 3.5 ml. of boiling water, 473 mg. of barium hydroxide octahydrate was added, and the resulting mixture heated gently under reflux for 35 minutes. An additional quantity of 3 ml. of water was then added, and heating continued 25 minutes. A small amount of insoluble material remaining was removed by filtration, the clear filtrate heated to boiling, carbon dioxide bubbled through the filtrate, and the barium carbonate resulting removed by filtration. Water was then removed by distillation *in vacuo* (4 mm.) and the residue dried in a vacuum desiccator over phosphorus pentoxide overnight. The crystalline residue was washed thoroughly with hot absolute ethanol to remove the retronecine present. The pure barium α-longinecate remaining was collected by filtration and dried in the air; yield 240 mg. That this salt was a monohydrate was demonstrated by determining the

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[8] Christie, Kropman, Novellie and Warren, *J. Chem. Soc.*, 1703 (1949).

[9] Adams and Govindachari, THIS JOURNAL, **71**, 1180 (1949).

[10] Kropman and Warren, *J. Chem. Soc.*, 2852 (1949).

[11] Kropman and Warren, *ibid.*, 700 (1950).

loss of weight upon heating 41.8 mg. at 100° *in vacuo* for 12 hours (calcd. loss, 2.04 mg.; found, 2.1 mg.).

The free α-longinecic acid was isolated by dissolving an exactly known quantity of the barium salt in water in a 10-ml. beaker, and then adding carefully, dropwise, with stirring 90% of the theoretical quantity of dilute sulfuric acid, the concentration of which had been accurately determined. After heating the resulting suspension gently for several minutes, the barium sulfate was removed by filtration. The filtrate was then extracted exhaustively with dry ether, and the combined ether extracts dried over anhydrous sodium sulfate. Upon solvent removal, the colorless residual oil obtained crystallized rapidly after standing briefly in a vacuum desiccator over phosphorus pentoxide. The yield of α-longinecic acid was 70 mg., m. p. 111–113° (cor.).

Hydrolysis of 521 mg. of seneciphylline by 494 mg. of barium hydroxide octahydrate was carried out in an identical manner, except that a reflux period of 40 minutes was employed, and no further addition of water was made. The yield of the barium salt was 122 mg. Liberation of the free acid gave 46 mg. of crude, crystalline residue, melting at 98–105°. Washing with a considerable volume of benzene at room temperature raised the melting range to 102–110°. This material was suspended in benzene, sufficient dry ether added to effect complete solution, and the resulting mixture permitted to evaporate slowly overnight. Scratching with a glass rod initiated a rapid crystallization of material melting at 100–108°; slow concentration of the benzene filtrate gave a slow crystallization leading to the purest isoseneciphyllic acid obtained; m.p. 110–111° (cor.); with softening at 108°. Upon admixture with α-longinecic acid melting at 111–113° (cor.), a melting point of 110–112° (cor.) was observed.

Summary

1. Evidence is presented which demonstrates conclusively the identity of the *Senecio* alkaloids seneciphylline and α-longilobine.

2. Isoseneciphyllic acid and α-longinecic acid have been shown to be identical.

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

The Effect of α-Methyl Substituents on the Anhydridization of Aliphatic Dibasic Acids

BY ROGER ADAMS AND JOHN L. ANDERSON[1,2]

Succinic and glutaric acids form cyclic anhydrides upon loss of water. The α-methylated succinic and glutaric acids are converted into cyclic anhydrides more readily than the unsubstituted acids, and the anhydrides are more stable. The ease of formation and stability of the anhydrides are proportional to the number of α-methyl groups present in the acids.[3] When adipic acid is dehydrated[4,5] it forms exclusively a polymeric anhydride. On the other hand, α,α,α′,α′-tetramethyladipic acid is converted exclusively under similar conditions to a cyclic monomer.[6]

This investigation was undertaken to determine the ease of dehydration of the α,α,α′,α′-tetramethyl substituted dibasic acids from pimelic to tetradecanedioic acids and to compare the products with those obtained from the corresponding unsubstituted acids.

Since the procedures described by Hill and Carothers[7] on the anhydridization of the unsubstituted high molecular weight acids with acetic anhydride or acetyl chloride were adopted, in this research their results are reviewed briefly. They observed that polymeric anhydrides (I) were obtained and that the molecular weights of the products were of the order of 3000–5000. They further investigated the behavior of these polymeric anhydrides under molecular distillation. To differentiate the various anhydrides, they proposed the following terminology which will be used in this Communication.

$$—(\mathrm{CO}—(\mathrm{CH_2})_n—\mathrm{COO})_x— \qquad \mathrm{I}$$

α-Anhydrides are the products prepared by the action of acetic anhydride or acetyl chloride on dicarboxylic acids.

β-Anhydrides (distillates) are the products of disproportionation of α-anhydrides upon heating in a molecular still. They are cyclic monomers or dimers.

γ-Anhydrides are the products formed from β-anhydrides on heating or on standing at room temperature. They are very similar to the α-modifications.

ω-Anhydrides are the residues of very high molecular weights remaining after the distillation of the β-anhydrides. They may be converted into β-anhydrides by continued molecular distillation.

The β-anhydrides obtained by molecular distillation of the α-anhydrides of adipic, pimelic, azelaic, undecanedioic, tridecanedioic, tetradecanedioic and octadecanedioic acids were unstable monomeric cyclic compounds (II) possessing the odors characteristic of the various ring sizes.[8]

$$\underline{\ulcorner(\mathrm{CO}\text{-}(\mathrm{CH_2})_n—\mathrm{COO})_x\urcorner}$$

II, $x = 1$; IIa, $x = 2$

The β-anhydrides derived from suberic, sebacic and dodecanedioic acids proved to be entirely dimeric (IIa) in nature.

The reaction of the anhydrides with aniline was used by these authors to determine the structures. Each anhydride group reacts very rapidly with aniline to form one anilide and one acid group. A linear or cyclic homopolymeric anhydride thus reacts with aniline to form three products (neglecting the effect of end groups): the dianilide, the monoanilide (anilic acid), and the dibasic acid in the fixed molar ratio 1:2:1 as determined

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[1] An abstract of a thesis submitted by Mr. John L. Anderson to the Graduate College of the University of Illinois, 1950, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] University of Illinois Predoctoral Fellow, 1948–1949; Allied Chemical and Dye Fellow, 1949–1950.

[3] Auwers and Meyer, *Ber.*, **22**, 2011 (1889); **23**, 101, 293 (1890).

[4] Voerman, *Rec. trav. chim.*, **23**, 265 (1904).

[5] Hill, THIS JOURNAL, **52**, 4110 (1930).

[6] Farmer and Kracovski, *J. Chem. Soc.*, 2318 (1926); 680 (1927).

[7] Hill and Carothers, THIS JOURNAL, **54**, 1569 (1932); **55**, 5023 (1933).

[8] Hill and Carothers, *ibid.*, **55**, 5039 (1933).