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Usaramoensine, the Alkaloid in *Crotalaria usaramoensis* E. G. Baker. Integerrimine from *Crotalaria incana* Linn and Senecionine from *Senecio glabellus* D. C. Stereochemical Relationships

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Crotalaria usaramoensis E. G. Baker affords a new alkaloid usaramoensine, stereoisomeric with senecionine and integerrimine. Usaramoensine gives upon hydrolysis with aqueous alkali retronecine and a new acid, usaramoensineic acid, stereoisomeric with senecic and integerrineic acids. By lactonization it gives integerrineic acid lactone. A careful infrared and ultraviolet absorption study of these acids and alkaloids has permitted the conclusion that usaramoensineic acid and senecic acid have the same configuration (*cis*) about the double bond and differ only in the configuration of the asymmetric carbon atom holding the hydroxyl. Integerrineic acid has the *trans*-configuration about the double bond and the hydroxyl group *cis* to the carboxyl with which it lactonizes. On the other hand the alkaloids, usaramoensine and integerrimine, have the same double bond configuration (*trans*) and senecionine the *cis* double bond configuration. Rearrangements in configuration of the double bond and of the asymmetric carbon holding the hydroxyl group during saponification of the alkaloids and during lactonization of the acids are discussed. Extraction of *Crotalaria incana* Linn and *Senecio glabellus* D. C. yielded integerrimine and senecionine, respectively.

In the continuation of a program of research on the alkaloids from *Senecio* and other species of plants which yield alkaloids of the *Senecio* type, three plants which have not been investigated previously, were examined.

The only alkaloids from *Crotalaria* species isolated up to now, monocrotaline¹ and dicrotaline² are similar to the typical *Senecio* alkaloids from *Senecio* species in that they yield on fission of the ester linkages a base, retronecine, and a dibasic acid, monocrotalic and dicrotalic acids. These two acids are substituted glutaric acids whereas the major alkaloids from *Senecio* species are substituted adipic acids. Two *Crotalaria* species, usaramoensine and incana, which have now been extracted, have yielded typical *Senecio* alkaloids.

Crotalaria incana Linn was found to contain integerrimine. It is the first plant investigated to yield integerrimine only. This alkaloid was isolated before as the minor constituent along with senecionine from *Senecio integerrimus* Nutt.³

Senecio glabellus D. C. yielded senecionine.

Extraction of *Crotalaria usaramoensis* E. G. Baker

(1) R. Adams and E. F. Rogers, *THIS JOURNAL*, **61**, 2815 (1939); R. Adams and T. R. Govindachari, *ibid.*, **72**, 158 (1950); R. Adams, B. L. Van Duuren, B. H. Braun, *ibid.*, **74**, 5608 (1952).

(2) J. S. C. Marais, *Onderstepoort J. Vet. Sci. Animal Ind.*, **20**, 61 (1944); R. Adams and B. L. Van Duuren, *THIS JOURNAL*, **75**, 2377 (1953).

(3) R. H. F. Manske, *Can. J. Research*, **17B**, 1 (1939).

gave a new alkaloid, C₁₈H₂₅O₅N, isomeric with the previously described *Senecio* alkaloids, senecionine and integerrimine. The new alkaloid, usaramoensine, showed a striking resemblance to senecionine and integerrimine in the infrared absorption spectrum which suggested a close similarity in structure.

Aqueous alkaline hydrolysis of usaramoensine afforded a base, retronecine, also obtained by the hydrolysis of the other C₁₈H₂₅O₅N *senecio* alkaloids, and a new crystalline dibasic acid, C₁₀H₁₆O₅, usaramoensineic acid. This acid is isomeric with senecic, integerrineic and a number of the other C₁₀ necic acids.

The various known C₁₀H₁₆O₅ necic acids, pertinent data concerning them and the alkaloids from which they were obtained, are found in Table I.

Vacuum sublimation of usaramoensineic acid at 120° and 1 mm. or evaporation with dilute hydrochloric acid gave a lactone, identical in melting point, specific rotation and analysis with integerrineic acid lactone.¹⁴ The lactone gave no depression of melting point on admixture with an authentic sample. The same lactone is obtained by lactonization of both senecic⁵ and integerrineic

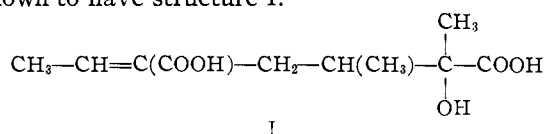
(14) This lactone has been given various names, e.g., senecic acid lactone, by previous investigators but will be called integerrineic acid lactone in this communication since we have shown that it has the same configuration as integerrineic acid.

TABLE I^{4a}
 STEREOISOMERIC NECIC ACIDS C₁₀H₁₆O₆

Alkaloid	Properties of alkaloids		M.p., °C. of picrate	Method of hydrolysis	Name	Necic acids	
	M.p., °C.	[α] _D				M.p., °C.	[α] _D
Senecionine ⁵	232-233	-55.8 ^{oa}	193-194	Aqueous alkali	Senecic acid	146 151 ¹¹	+10.95 ^{ob}
Integerrimine ³	172	+4.3 ^o +2.7 ^{oc,d}	224 ^d	Ethanolic alkali	Integerrineic acid	151	+15.9 ^{ob,d} +18.0 ^{o10,b}
Usaramoensine ^d	221	-25.2 ^{oa}	235	Aqueous alkali	Usaramoensineic acid	170	+6.66 ^{ob}
Squalidine ⁷	169	-26.9 ^{oa}	203	Ethanolic alkali	Squalineic acid
Hieracifoline ^{6,8}	227	-89.7 ^{oa}	Ethanolic alkali	Hieracineic acid	131-132
Platyphylline ⁹				Aqueous alkali	Platynecic acid	133-135
				Ethanolic alkali	Senecic acid	151-152

^a Chloroform. ^b Ethanol. ^c Methanol. ^d Present investigation.

acids.¹⁰ The lactone on hydrolysis always gave only integerrineic acid.¹⁰ Senecic acid has been shown to have structure I.¹⁰



Kropman and Warren¹¹ noted that the ultraviolet absorption spectra of senecic and integerrineic acids were different and ascribed this to *cis-trans* isomerism by analogy to retroneic and isatineic acids.^{12,13} They suggested that senecic acid was the *cis*-acid corresponding to isatineic acid, and integerrineic acid the *trans*-acid corresponding to retroneic acid. Danilova and Konovalova⁹ proposed that *cis-trans* isomerism will account for the isolation of two isomeric acids from platyphylline depending on the method used in the hydrolysis of the alkaloid.

The isolation of a third acid, usaramoensineic acid, isomeric with senecic and integerrineic acids and which gives the same lactone, necessitated a reinvestigation of the whole problem of the stereochemistry of the C₁₀ necic acids. The only isomerism considered by the previous workers was the geometrical isomerism about the carbon-carbon double bond. It is clear, however, that structure I can exist in four stereoisomeric forms, *i.e.*, four *dl*-pairs. Senecic, integerrineic and usaramoensineic acids from three of the *dl*-pairs would account for three of the eight possible optically active forms. In order to obtain more evidence regarding the stereochemical relationship between senecic, integerrineic and usaramoensineic acids, the infrared and ultraviolet absorption spectra of these three acids, their parent alkaloids and of tiglic and angelic acids were studied.

(4a) Except for platyphylline, molecular formula C₁₀H₁₇O₆N, all the alkaloids in this table have the molecular formula C₁₀H₁₅O₆N and yield retroneic acid on hydrolysis. Platyphylline yields the base platynecine.

(5) R. Adams and T. R. Govindachari, *THIS JOURNAL*, **71**, 1953 (1949).

(6) W. C. Evans and E. T. Rees, *Nature*, **164**, 30 (1949).

(7) G. Barger and J. J. Blackie, *J. Chem. Soc.*, 743 (1936).

(8) R. H. F. Manske, *Can. J. Research*, **17B**, 8 (1939).

(9) A. V. Danilova and R. A. Konovalova, *Doklady Akad. Nauk., S.S.S.R.*, **73**, 315 (1950).

(10) M. Kropman and F. L. Warren, *J. Chem. Soc.*, 700 (1950).

(11) M. F. Richardson and F. L. Warren, *ibid.*, 452 (1943).

(12) S. M. H. Christie, M. Kropman, E. C. Leisegang and F. L. Warren, *J. Chem. Soc.*, 1700 (1949).

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

Previous investigations have indicated that differences do exist between the ultraviolet absorption spectra of *cis* and *trans* unsaturated acids.¹⁴ Thus, the absorption curve for elaidic acid is shifted approximately 4 mμ toward the visible end of the spectrum and the maximum absorption is increased about 15% as compared to oleic acid. For the compounds under investigation, however, tiglic and angelic acids seemed the most logical *cis-trans* pair to be used as models.

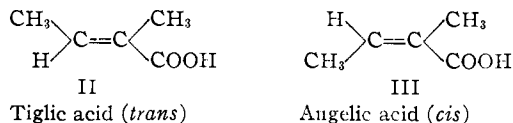
The extinction maximum for tiglic acid was found to be considerably higher than that for angelic acid and the wave length of maximum absorption of tiglic acid was shifted 4 mμ. The ultraviolet absorption data are given in Table II.

 TABLE II
 ULTRAVIOLET ABSORPTION DATA

Compound	Geo- metric con- figura- tion	λ _{max} (mμ)		a	ε _{max}	
		a	b		a	b
Angellic acid	<i>cis</i>	216	9,500
Tiglic acid	<i>trans</i>	212	13,500
Senecic acid	<i>cis</i>	215	218, ¹⁵ 215 ¹⁰	6,195	4950, ¹⁵ 4100 ¹⁰
Usaramoensineic acid	<i>cis</i>	215	5,977
Integerrineic acid	<i>trans</i>	214	218, ¹⁵ 218 ¹⁰	9,021	9250, ¹⁵ 9333 ¹⁰
Senecionine	<i>cis</i>	215	2,400
Integerrimine	<i>trans</i>	212	216 ¹⁵	10,900	8000 ¹⁵
Usaramoensine	<i>trans</i>	203	12,700
Integerrineic acid lactone	<i>trans</i>	222 ¹⁵	12,000 ¹⁵

^a This investigation: solvent, 95% ethanol. ^b Previous investigations: solvent, distilled water.

If, in view of the extensive chemical evidence provided by previous workers,¹⁷ tiglic acid is taken to have the *trans*-structure II, and angelic acid the *cis*-structure III, then on the basis of their ultraviolet



(14) I. I. Rosoff, T. K. Platt, H. B. Klevens and G. O. Burr, *THIS JOURNAL*, **67**, 673 (1945).

(15) E. C. Leisegang, *J. S. Afr. Chem. Inst.*, **3**, 73 (1950).

(16) These values are in accord with those previously reported for α,β-unsaturated lactones [V. Wenner and T. Reichstein, *Helv. Chim. Acta*, **27**, 24 (1944)].

(17) M. Pfeiffer, *Z. Physik. Chem.*, **48**, 58 (1904); J. J. Sudborough and M. J. P. Davies, *J. Chem. Soc.*, **95**, 976 (1909); K. V. Auwers and H. Wissenbach, *Ber.*, **56**, 723 (1923); D. H. Hey, *J. Chem. Soc.*, 2321 (1928).

let spectra, the other acids may be assigned the geometrical configurations given in Table II.

Further support for the configurations assigned to the acids was obtained from the infrared absorption data. The significant bands and their relative intensities are given in Table III.

TABLE III
INFRARED ABSORPTION DATA OF ACIDS IN CHLOROFORM SOLUTION

	Geometric configuration	Absorption due to C=C (wave numbers)	Intensity of band
Angelic acid	<i>cis</i>	1645	Medium-strong
Tiglic acid	<i>trans</i>	1650	Strong
Usaramoensineic acid	<i>cis</i>	No absorption
Senecic acid	<i>cis</i>	1635	Very weak
Integerrineic acid	<i>trans</i>	1645	Strong
Integerrineic acid lactone	<i>trans</i>	1645	Strong

The infrared absorption spectra of the compounds assigned *cis*-configurations on the basis of ultraviolet absorption data show very weak bands in the C=C region. Usaramoensineic acid shows no band at all in this region in chloroform solution, but when the infrared absorption spectrum of the acid was determined in Nujol mull, a very weak band in the C=C region did appear. The corresponding *trans* compounds show strong bands. The same relationship holds for tiglic and angelic acids. The previously published⁵ infrared absorption spectra of senecic acid (*cis*) and integerrineic acid lactone (*trans*) in Nujol mull also indicates clearly this difference in intensity of the C=C bands, senecic acid showing a weak band and integerrineic acid lactone a very strong band.

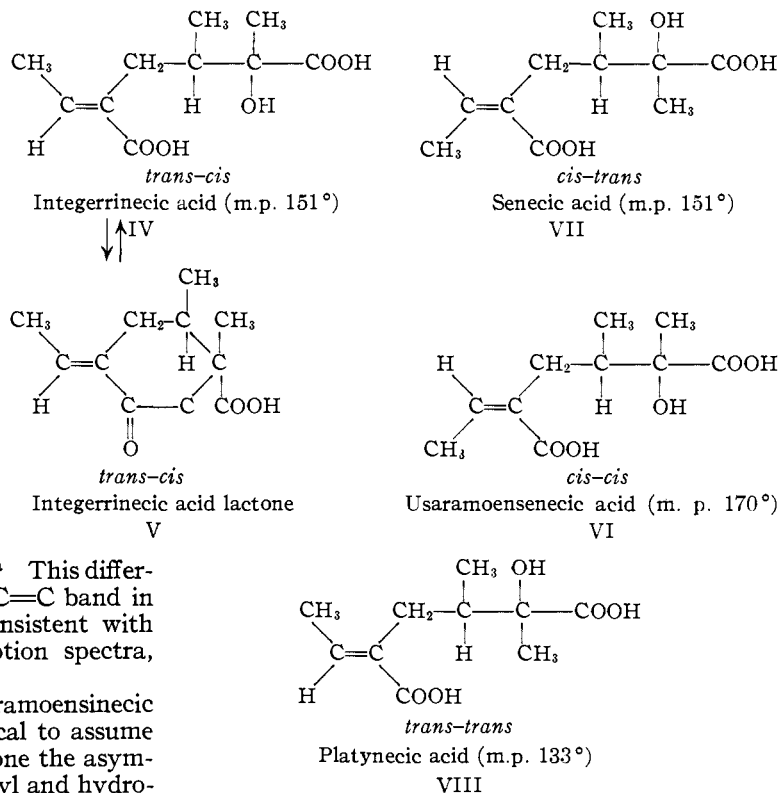
From the data in Table III it will also be seen that there is a slight shift, 5 to 10 wave numbers, in the position of the C=C band in going from the *cis* to the *trans* compounds.^{17a} This difference in intensity and position of the C=C band in the infrared absorption spectra is consistent with the results of the ultraviolet absorption spectra, previously discussed.

Since senecic, integerrineic and usaramoensineic acids give the same lactone it is logical to assume that in all three acids and in the lactone the asymmetric carbon atom holding the methyl and hydrogen, designated the β -carbon, has the same configuration. From this it follows that senecic acid

(17a) The shift in the position of the C=C stretching band has been used previously in the determination of the geometrical configurations of the 2-octadecenoic acids. The *cis* acid shows a C=C band at 1640 cm.⁻¹ [G. S. Myers, THIS JOURNAL, **73**, 2100 (1951); R. G. Sinclair, A. F. McKay, G. S. Myers and R. N. Jones, *ibid.*, **74**, 2578 (1952)]. The shift is analogous to that found in Raman spectra studies of the frequency of the C=C band in unsaturated carbonyl compounds [G. V. N. L. Murty and T. S. Seshadri, *Proc. Indian Acad. Sci.*, **11A**, 424 (1940)].

and usaramoensineic acid both of which have the *cis*-configuration about the double bond differ only in the configuration about the asymmetric carbon atom holding the methyl, carboxyl and hydroxyl groups, designated the α -carbon atom. In integerrineic acid this α -carbon will have its hydroxyl *cis* to the lactonizing carboxyl (IV), since the acid and lactone are interconvertible. Integerrineic acid lactone can be represented by structure V. In the other two acids the hydroxyl of the α -carbon may be *cis* or *trans* VI or VII with inversion of configuration taking place in one of these acids during lactonization. The conditions causing lactonization of senecic and usaramoensineic acids cause also a change in the configuration about the C=C from the *cis* to the *trans* form.

Danilova and Konovalova⁹ isolated by the aqueous alkaline hydrolysis of platyphylline a new acid, platynecic acid,¹⁸ C₁₀H₁₆O₆, isomeric with senecic acid (see Table I). It lactonizes to integerrineic acid lactone. This acid is probably the fourth isomeric stereoisomeric acid with the *trans-trans* structure VIII. If this is accepted to be the case a comparison of the melting points of the four acids is of interest, even though melting point comparisons for assignment of structures are often unreliable. Since integerrineic acid (IV) with



the hydroxyl *cis* to the carboxyl with which it lactonizes, melts higher than platynecic acid (VIII) with the hydroxyl *trans* to the carboxyl with which it lactonizes, then the lower melting compound, senecic acid (VII), of the *cis*-geometric pair might be tentatively assumed to have its hydroxyl *trans* and usaramoensineic acid (VI) its

(18) The name platynecic acid was previously also used for the compound referred to as integerrineic acid lactone in this paper.

hydroxyl *cis* to the carboxyl with which each lactonizes.

Manske⁸ reported the isolation of hieracineic acid, C₁₀H₁₆O₅, isomeric with senecic acid and with approximately the same melting point as that of platynecic acid. This acid may be identical with platynecic acid obtained by the Russian workers.⁹

The infrared absorption spectra of the alkaloids show, both in mull and in chloroform solution, Fig. 1, the same notable shift in the position of the C=C absorption band as was described above for the acids and the lactone. Thus, in chloroform solution, integerrimine and usaramoensine show a strong band at 1665 cm.⁻¹ and senecionine a band at 1645 cm.⁻¹. Again the infrared evidence is in accord with the ultraviolet evidence (Table II) from which it may be concluded that the geometric configuration about the C=C of the unsaturated diesters in the alkaloid structures are *trans* in integerrimine and usaramoensine and *cis* in senecionine. Retronecine shows no absorption in the C=C region in chloroform solution (Fig. 1), so need not be considered a factor in the absorption spectra of the alkaloids in which it is present.

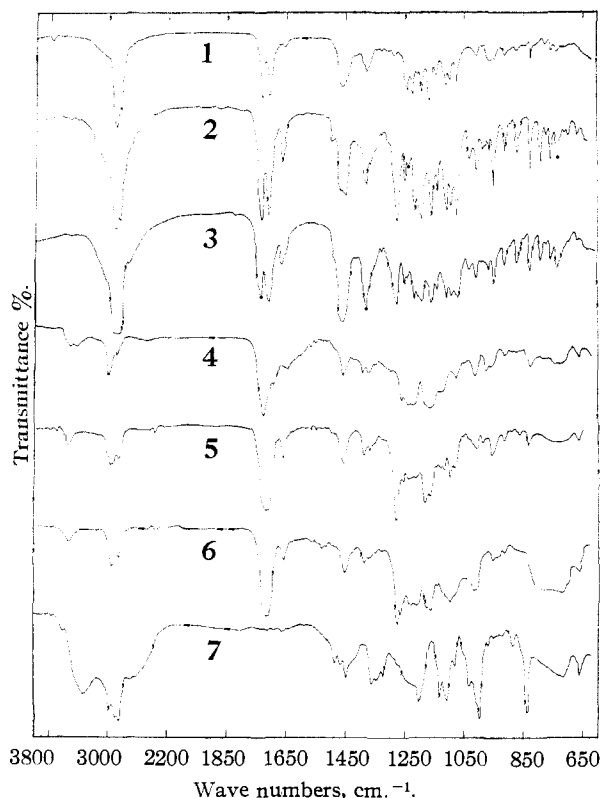


Fig. 1.—Infrared absorption spectra: 1 and 4, senecionine; 2 and 5, integerrimine; 3 and 6, usaramoensine; 7, retronecine; 1-3: Nujol mull; 4-6: 2.5% chloroform solution, 0.2-mm. matched cell; 7: 5% chloroform solution, 0.1-mm. matched cell.

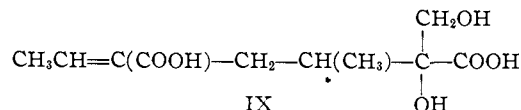
From these data it may be deduced that the acid isolated by the hydrolysis of any of these alkaloids need not occur in the same stereochemical form in the alkaloid and that the *cis*-form does not always occur in the alkaloid as postulated by Warren, *et al.*¹⁰ This is borne out by the fact that the stereo-

chemical configuration of the acid obtained varies with the method of hydrolysis. This was noticed in the case of the hydrolysis of platyphylline⁹ (see Table I) and also for retrorsine and isatidine.^{13,14}

From spectral data on the alkaloids it may also be concluded that integerrimine and usaramoensine differ only in the configuration about the α -carbon atom whereas they both differ from senecionine, at least in the configuration about the C=C of the unsaturated diester part of the alkaloid molecule.

In view of the results described above, several other conclusions of previous investigators must be reconsidered. Thus Kropman and Warren¹⁰ suggested that integerrimine and squalidine are identical. A direct comparison of these alkaloids was not performed. However, a study of the data presented in Table I indicates that this cannot be the case in view of the wide difference in rotations of these alkaloids. The picrate of integerrimine, not previously reported, was prepared during this investigation and has a melting point quite different from that reported for squalidine (see Table I). The position of squalidine in the general picture outlined above cannot be determined until material is available for further investigation. A difference in the orientation of the acid moiety in the alkaloid or a shifting of the double bond is also not excluded.

A reinvestigation of the results described by Warren and co-workers^{13,14} and de Waal¹⁹ on the isomerism of isatineic and retronecic acids (IX) is



also now desirable. In the case of the senecic acid structure (I) four *dl*-pairs are possible and in the retronecic acid structure the same conditions obtain. Isatineic acid as isolated by Warren¹³ was optically inactive whereas de Waal¹⁹ reports an optically active acid. Also, the reported optical rotations for retronecic acid, tabulated by Warren, *et al.*,¹³ vary between -11.4 and $+58^\circ$ which indicates clearly that different stereoisomeric acids were obtained on different occasions. The probability of stereoisomerism due to the presence of the two asymmetric carbon atoms must not be overlooked in these acids.

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

Experimental

All melting points are corrected.

Isolation of Usaramoensine.—The alkaloid was obtained by extraction of the seeds of *Crotalaria usaramoensis* E. G. Baker by using the previously described procedure of Adams and Rogers.¹ The crude alkaloid, m.p. $178-181^\circ$, was recrystallized several times from acetone; colorless prisms, m.p. (sealed evacuated tube) 221° (dec.).

Anal. Calcd. for C₁₈H₂₅O₅N: C, 64.48; H, 7.57; N, 4.28. Found: C, 64.43; H, 7.52; N, 4.28.

(19) H. L. de Wall, *Onderstepoort J. Vet. Sci. Animal Ind.*, **14**, 445 (1940).

Rotation.—0.0473 g. of alkaloid made up to 10 ml. in chloroform at 28° gave $\alpha_D -0.120^\circ$; l 1, $[\alpha]^{25}_D -25.2^\circ$ ($\pm 1.0^\circ$).

Usaramoensine Picrate.—The picrate, prepared from equivalent amounts of alkaloid and picric acid in methanol, was recrystallized from methanol, m.p. 235° (dec.).

Anal. Calcd. for $C_{15}H_{25}O_5N \cdot C_6H_3O_7N_3 \cdot CH_3OH$: C, 50.33; H, 5.36; N, 9.40; loss of CH_3OH , 8.0 mg. Found: C, 50.37; H, 5.16; N, 9.70; loss of CH_3OH , 7.3 mg.

Hydrolysis of Usaramoensine.—Hydrolysis of the alkaloid with aqueous barium hydroxide by the previously described procedure¹ yielded: (a) **Retronecine.**—The base was purified by recrystallization from acetone; m.p. 121°, not depressed on admixture with an authentic sample. Retronecine picrate, m.p. 141°, was prepared from the base and gave no depression on admixture with an authentic specimen, m.p. 141° (lit.²⁰ m.p. 141–143°).

(b) **Usaramoensineic Acid.**—The crystalline acidic cleavage product from the hydrolysis was purified to constant melting point and rotation by recrystallization from ethyl acetate. Prisms, m.p. 170°, were obtained.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.40. Found: C, 55.92; H, 7.05.

Rotation.—0.0360 g. made up to 1.60 ml. in 95% ethanol at 25° gave $\alpha_D +0.150^\circ$; l 1, $[\alpha]^{25}_D +6.66^\circ$ ($\pm 2.0^\circ$).

Lactonization of Usaramoensineic Acid.—A solution of 50 mg. of usaramoensineic acid in 2 ml. of dilute hydrochloric acid was evaporated to dryness on a steam-cone. The treatment was repeated once more. The resultant oil crystallized on standing in a vacuum desiccator and was recrystallized from benzene; m.p. 151°.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.59; H, 7.06.

Rotation.—0.0100 g. made up to 1.59 ml. in 95% ethanol at 27° gave $\alpha_D +0.320^\circ$; l 1, $[\alpha]^{27}_D +50.8^\circ$ ($\pm 0.5^\circ$).

This product gave no depression of melting point on admixture with integerrineic acid lactone, m.p. 152–153°, obtained by lactonization of senecioic acid from *Senecio cineraria*. Integerrineic acid lactone could also be obtained by vacuum sublimation of usaramoensineic acid at 120° and 1 mm.

Isolation of Integerrimine.—The alkaloid was obtained by extraction of the seeds of *Crotalaria incana* Linn and isolated in the usual manner. The crude alkaloid, m.p. 164–165°, was purified to constant rotation and melting point by recrystallization from acetone, m.p. 170–171° (lit.³ m.p. 172°).

Anal. Calcd. for $C_{18}H_{25}O_5N$: C, 64.48; H, 7.57; N, 4.28. Found: C, 64.48; H, 7.41; N, 4.32.

Rotation.—0.055 g. made up to 5 ml. in methanol at 27° gave $\alpha_D +0.030^\circ$; l 1, $[\alpha]^{27}_D +2.7^\circ$ ($\pm 1^\circ$).

Integerrimine Picrate.—The picrate prepared from equivalent amounts of alkaloid and picric acid in methanol

was purified by recrystallization from the same solvent, m.p. 224°.

Anal. Calcd. for $C_{18}H_{25}O_5N \cdot C_6H_3O_7N_3$: C, 51.06; H, 4.99; N, 9.92. Found: C, 50.79; H, 4.99; N, 10.02.

Hydrolysis of Integerrimine: Integerrineic Acid. The alkaloid was hydrolyzed with methanolic alkali as described by Manske⁹ and the base and acid isolated by the usual procedure. The base was identified as retronecine by melting point and the melting points of mixtures of the base and its picrate with authentic samples. The acid was recrystallized from ethyl acetate, m.p. 149–150°.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.40. Found: C, 55.60; H, 7.05.

Rotation.—0.0215 g. made up to 5 ml. in ethanol at 28° gave $\alpha_D +0.068^\circ$; l 1, $[\alpha]^{28}_D +15.9^\circ$ ($\pm 1.0^\circ$).

Integerrineic Acid Lactone.—Vacuum sublimation of integerrineic acid at 120° and 1 mm. gave integerrineic acid lactone, m.p. 153°. This substance gave no depression of melting point on admixture with an authentic sample.

Isolation of Senecionine.—Extraction of *Senecio glabellus* D. C. (whole plant) by the usual procedure yielded senecionine only. The crude alkaloid (yield 0.075%) was purified to constant rotation and melting point by recrystallization from acetone; m.p. (sealed evacuated tube) 236–237° (dec.).

Anal. Calcd. for $C_{18}H_{25}O_5N$: C, 64.48; H, 7.57; N, 4.28. Found: C, 64.49; H, 7.59; N, 4.17.

Rotation.—0.0278 g. made up to 5 ml. in chloroform at 30° gave $\alpha_D -0.310^\circ$; l 1, $[\alpha]^{30}_D -55.8^\circ$ ($\pm 0.5^\circ$).

The infrared absorption spectrum of the alkaloid was identical with that of an authentic sample of senecionine from *Senecio cineraria*. The alkaloid and its picrate, m.p. 193–194°, gave no depression on admixture with authentic specimens.

Tiglic Acid.—Tiglaldehyde (Eastman Kodak Co.) was oxidized with silver oxide in water by the procedure previously described for the oxidation of acrolein to acrylic acid.²¹ The acid was purified by steam distillation followed by crystallization from petroleum ether (b.p. 30–60°); m.p. 65° (lit.²² m.p. 65°).

Angelic Acid.—This acid was prepared from tiglic acid by the method of Kaufmann and Kuchler²³ by bromination, dehydrohalogenation followed by reduction with sodium amalgam. The acid was purified by recrystallization from petroleum ether (b.p. 30–60°); m.p. 45° (lit.²³ m.p. 45°).

Ultraviolet Absorption Spectra.—The ultraviolet spectra were obtained with a Cary automatic recording spectrophotometer.

Infrared Absorption Spectra.—The infrared spectra were obtained with a Perkin-Elmer automatic recording infrared spectrometer equipped with rock salt optics.

URBANA, ILLINOIS

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(22) R. E. Buckles and G. V. Mock, *J. Org. Chem.*, **15**, 680 (1950).

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(20) R. A. Konvalova and A. P. Orekhov, *Bull. soc. chim.*, [5] **4**, 2037 (1937).