organic solvents. It was recrystallized from water containing a few drops of methanol. The crystallization was very slow and had to be induced by scratching. After another recrystallization from the same solvent, the product melted at 113° (cor.).

*Anal.* Calcd. for $C_{19}H_{31}O_5N$: C, 64.57; H, 8.84. Found: C, 64.39; H, 8.79.

**Hydrolysis of Tetrahydrosenecionine.**—A solution of 0.13 g. of tetrahydrosenecionine in 2 ml. of water was hydrolyzed by refluxing with 0.25 mg. of barium hydroxide octahydrate for one hour. The acid and basic portions were isolated by the usual procedure.

**Acid Portion.**—A yield of 60 mg. of the crude acid was obtained. The crystallization proved difficult and the acid was therefore lactonized to the more easily crystallized senecic acid lactone which was purified by two recrystallizations from benzene. The product, m. p. 155–156° (cor.), was identical with that obtained by direct hydrolysis of senecionine, followed by lactonization.

**Hydrogenolysis of Senecionine (Platinum Oxide Catalyst).**—A solution of 0.2 g. of senecionine in 15 ml. of absolute ethanol was hydrogenated in the presence of 0.2 g. of platinum oxide catalyst. The first two mole equivalents of hydrogen were taken up in less than thirty minutes, after which the reduction slowed down considerably. The total volume of hydrogen absorbed after a further period of ten hours was 39 ml. (N. T. P.), the volume required by theory for three mole equivalents being 40.1 ml. After filtering off the catalyst, the solvent was removed *in vacuo*, leaving 200 mg. of a glassy transparent mass, which could be reduced to a powder. The product was extremely hygroscopic and was easily soluble in water and ethanol, but insoluble in all non-polar solvents. Attempts to crystallize this material or the product obtained from it by the action of diazomethane were unsuccessful.

A solution of 0.35 g. of this reduction product was hydrolyzed by refluxing in 8 ml. of water with 1 g. of barium hydroxide octahydrate for one hour. The acid portion isolated in the usual way was a colorless oil. The yield was 0.18 g. This was methylated by diazomethane and the ester purified by distillation at 0.1 mm. pressure, $n^{20}D$ 1.4595. The infrared spectrum contained all the absorption bands characteristic of dihydrosenecic acid dimethyl ester, but there were a few extraneous absorptions which could be accounted for only by impurities.

*Anal.* Calcd. for $C_{12}H_{22}O_5$: C, 58.55; H, 9.01. Found: C, 58.71; H, 8.84.

## Summary

1. The alkaloid isolated from *Senecio cineraria* in this Laboratory from seeds obtained from Holland has been shown to be senecionine.

2. On hydrolysis with baryta senecionine gives one molecule of retronecine and one molecule of a dibasic acid $C_{10}H_{16}O_5$, senecic acid.

3. Senecic acid was easily lactonized to a crystalline lactonic monobasic acid, $C_{10}H_{14}O_4$, senecic acid lactone, reported by previous investigators as the necic acid from senecionine.

4. On reduction with hydrogen in the presence of Raney nickel, senecionine absorbs two moles of hydrogen to form tetrahydrosenecionine which has the properties of an amino acid and yields on hydrolysis retronecanol and senecic acid. The methyl ester of this compound was also characterized. In the presence of platinum oxide catalyst, senecionine absorbs three moles of hydrogen, yielding an amorphous product, which gives on hydrolysis retronecanol and dihydrosenecic acid.

5. Senecionine is therefore a cyclic diester from one molecule of retronecine and one molecule of a dibasic acid, each of the two hydroxyls in retronecine being involved in ester formation.

URBANA, ILLINOIS RECEIVED FEBRUARY 11, 1949

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

# Senecio Alkaloids: The Alkaloids of *Senecio Douglasii, Carthamoides, Eremophilus, Ampullaceus* and *Parkşii*

BY ROGER ADAMS AND T. R. GOVINDACHARI

In a previous communication,[1] the isolation of two alkaloids, designated as α- and β-longilobine from *Senecio longilobus* by application of a chromatographic procedure, was described. The β-longilobine fractions from the chromatograms were contaminated with another alkaloid, which was not isolated in a pure condition but tentatively identified as riddelliine on the basis of its infrared spectrum.

In the course of work carried out in this laboratory over a period of years, several *Senecio* alkaloids had been isolated. Of these, the alkaloids from *Senecio douglasii, carthamoides, eremophilus* and *ampullaceus* had specific rotations ranging from −86 to −109° and melting points ranging from 212 to 218°. The analytical values on these alkaloids corresponded roughly to the molecular formula $C_{18}H_{23}O_5N$, but satisfactory values were not obtained, even after repeated crystallization. All these alkaloids gave infrared spectra which were essentially identical with that of the total alkaloid from *Senecio longilobus* before separation into its constituents. A sample of senecionine from *Senecio vulgaris*,[2] kindly supplied by Dr. R. H. F. Manske, also gave the same infrared spectrum. The slight differences among these spectra were such as would be expected when the proportions of the components of a mixture were varied. The infrared spectra were not changed in any way by repeated crystallization. It was evident that these alkaloids were mixtures which could not be separated into the components by mere crystallization procedures. It was considered that the chromatographic method applied successfully in the isolation of α- and β-longilobine could profitably be extended to these other alkaloids. As a result of this work, it has been established that in addition to varying amounts of the three alkaloids

(1) Adams and Govindachari, THIS JOURNAL, **71**, 1180 (1949).

(2) Manske, *Can. J. Res.*, **14B**, 8 (1936).

present in *Senecio longilobus*, all these alkaloids have a fourth component closely associated with α-longilobine, which has been positively identified as senecionine.

In identifying the components of the mixture of alkaloids encountered in this investigation, especially when complete separation by chromatography proved difficult, extensive use has been made of infrared spectra. The strong absorption bands of α- and β-longilobine, senecionine and riddelliine were common to more than one of these due to the presence in all four of a retronecine moiety and of carbonyl linkages. It was, therefore, necessary to use comparatively weak bands for identification. The characteristic bands used were at 992 cm.$^{-1}$ and 902 cm.$^{-1}$ for α-longilobine, 1055 cm.$^{-1}$ for β-longilobine, 757 cm.$^{-1}$ for senecionine and 1120 cm.$^{-1}$ for riddelliine. The hydroxyl band at 3590 cm.$^{-1}$ was common to both β-longilobine and riddelliine.

From *Senecio douglasii*, the presence of senecionine was detectable only in the α-longilobine fraction and not in the total alkaloid, while from *Senecio carthamoides*, *eremophilus*, *ampullaceus* and *vulgaris*, the total alkaloids all showed the characteristic senecionine absorption at 757 cm.$^{-1}$. The riddelliine bands were not noticeable in any of the total alkaloids but only in the fractions eluted from the alumina after removal of the main α-longilobine fraction. On the basis of the chromatographic separation of constituents and infrared data on the original alkaloids and the fractions, the estimated composition of the alkaloids from *Senecio longilobus*, *douglasii*, *carthamoides*, *eremophilus* and *ampullaceus* are given in Table I.

TABLE I

| Source | α-Longilobine fraction % | β-Longilobine fraction % |
|---|---|---|
| *S. longilobus* | 60 .. | 40 (some riddelliine) |
| *S. douglasii* | 35 .. | 65 (some riddelliine) |
| *S. carthamoides* | 90 (some senecionine) | nil .. |
| *S. eremophilus* | 80 (some senecionine) | 20 (some riddelliine) |
| *S. ampullaceus* | 70 (some senecionine) | 20 .. |

It is noteworthy that the difference in molecular structure of the pair α-longilobine ($C_{18}H_{23}O_5N$) and senecionine ($C_{18}H_{25}O_5N$) consists in two carbon–carbon double bonds in the acid moiety of the first and only one in the latter. Exactly the same difference exists in the second pair, riddelliine ($C_{18}H_{23}O_6N$) and β-longilobine ($C_{18}H_{25}O_6N$). Although the chromatographic separation of the individuals in these pairs proved difficult, the isolation of one pair from the other was simple due to the greater adsorption affinity for alumina of riddelliine and β-longilobine over α-longilobine and senecionine. Apparently the additional hydroxyl group in the former pair causes this difference. These four alkaloids have the same basic moiety, retronecine. Since they are very similar to each other in properties and appear together in several species of *Senecio*, it is probable that they are closely related structurally. The dibasic acid moieties in each probably have the same skeleton, α-longinecic acid ($C_{10}H_{14}O_5$) with two double bonds and one hydroxyl, senecic acid ($C_{10}H_{16}O_5$) with one double bond and one hydroxyl, riddellic acid ($C_{10}H_{14}O_6$) with two double bonds and two hydroxyls and β-longinecic acid ($C_{10}H_{16}O_6$) with one double bond and two hydroxyls. Moreover, the acids containing two double bonds have one of these in conjugation with a carboxyl, the other being in an isolated position in the molecule. In the acids containing only one double bond, this bond is in conjugation with one of the carboxyl groups.

**The Alkaloids of *Senecio Douglasii*.**—When the alkaloidal fraction from *Senecio douglasii* was submitted to repeated crystallization from ethanol, there was very little difference in specific rotation and melting point from the fifth to the seventeenth crystallization, although the analysis corresponded more closely to the empirical formula $C_{18}H_{23}O_5N$. The infrared spectrum of the product recrystallized seventeen times still showed the strong absorption band at 1055 cm.$^{-1}$ characteristic of β-longilobine ($C_{18}H_{25}O_6N$) and also the hydroxyl band at 3590 cm.$^{-1}$ which is common to β-longilobine and to riddelliine.[3a,b] On hydrolysis the alkaloid furnished an impure acid, which after a tedious crystallization procedure furnished a small amount of acid melting at 145° ($C_{10}H_{16}O_6$).

The total alkaloid from *Senecio douglasii* was easily separated into two fractions corresponding to α- and β-longilobine on passing a chloroform solution through an alumina column and developing and eluting with chloroform containing ethanol. The portion recovered from the filtrate was found to consist mainly of α-longilobine associated with some amount of another alkaloid with a lower specific rotation. The amount of this component was too small to make its isolation feasible. It is very likely from examination of infrared spectra that this component is senecionine. By repeated chromatographic fractionation, involving the rejection of certain early filtrates rich in senecionine, it was possible to isolate α-longilobine in an optically pure condition, identical in melting point and specific rotation, and yielding the same necic acid as the product from *Senecio longilobus*.

The alumina column was divided arbitrarily into three sections and the adsorbed materials isolated by elution with *N* acetic acid followed by basification and extraction with chloroform. The lower third of the column thus yielded almost pure β-longilobine, which was purified by further chromatographic fractionation. β-Longilobine was obtained in optically pure condition, identical in melting point and specific rotation and yielding the same necic acid as the product from *Senecio longilobus*. The material recovered from the top third of the column had a specific rotation of approximately −65 to −70°. Examination of the

(3) (a) Manske, *Can. J. Res.*, **17B**, 1 (1939); (b) Adams, Hamlin, Jelinek and Phillips, THIS JOURNAL, **64**, 2760 (1942).

infrared spectrum revealed that it was composed essentially of β-longilobine. Hydrolysis of this fraction gave β-longinecic acid. The higher specific rotation of this fraction appeared to be caused by contamination with riddelliine ($[\alpha]_D$ −109°). The infrared spectrum of an artificial mixture of pure β-longilobine and pure riddelliine simulated the infrared spectrum of this fraction very closely.

**The Alkaloids of *Senecio Carthamoides*.**—On passing the alkaloid from *Senecio carthamoides* in chloroform solution and developing with chloroform, the early fractions in the filtrate contained a low-rotating component, which was closely followed by the main α-longilobine fraction. By introducing the material in benzene–chloroform mixture (80–20) and developing with large volumes of the same solvent mixture, gradually increasing the chloroform content, the low-rotating component was isolated in a pure condition, and identified as senecionine by comparison with an authentic specimen. The isolation of α-longilobine, in its optically pure form, proved to be exceedingly difficult because of its persistent association with senecionine. The purest α-longilobine that could be obtained in fair quantity to permit further examination had a specific rotation of −115°, ten degrees lower than that of pure α-longilobine. However, there was little doubt from the evidence of infrared spectra, analytical data, melting point determinations and melting points of mixtures of the alkaloid and its methiodide with authentic specimens and hydrolysis to an acid $C_{10}H_{14}O_5$ identical with α-longinecic acid that it was essentially pure α-longilobine.

When the chromatographic column was developed and eluted by chloroform followed by chloroform containing one per cent. ethanol, instead of in benzene–chloroform mixtures employed for the isolation of senecionine (Table III), approximately 10% of the material was left adsorbed on the alumina. This material had a specific rotation of −96°. Examination of the infrared spectrum revealed that it was an impure mixture of α-longilobine and senecionine. No β-longilobine or riddelliine could be detected.

**The Alkaloids of *Senecio Eremophilus*.**—The crude alkaloid from *Senecio eremophilus* behaved on chromatography essentially in the same way as that from *Senecio carthamoides* as far as the α-longilobine and senecionine fractions were concerned. Senecionine was present in significant amounts and was isolated in a pure condition. It was not possible to isolate α-longilobine in its optically pure form as it was always associated with some senecionine, in spite of repeated fractional chromatography. When the fractions corresponding to α-longilobine with specific rotations of approximately −100° were passed again through alumina columns, the early filtrates always contained senecionine, but fractions with a higher specific rotation than the starting material were isolated only in trace amounts. Since examination of the infrared spectra of the various fractions from such a chromatogram showed that only α-longilobine and senecionine were present and gave no evidence of structural change or decomposition, the facts are difficult to explain. The presence of β-longilobine in the crude alkaloid from *S. eremophilus* was established by its actual isolation in optically pure condition by the usual procedure. The product was identical in every respect with that isolated from *S. longilobus* and gave the same necic acid, m. p. 146° on hydrolysis.

**The Alkaloids of *Senecio Ampullaceus*.**—The alkaloidal fraction from *Senecio ampullaceus* was isolated in low yield (0.025%) and a total of 0.5 g. was available. On hydrolysis with baryta, this material furnished retronecine and an acid which could not be purified. The crude alkaloid was passed in chloroform solution through an alumina column and continuously washed with chloroform. The main fraction passing into the filtrate had a specific rotation of −100°, giving an infrared spectrum essentially identical with that of α-longilobine associated with some senecionine. Further purification was not undertaken because of the proved difficulty of separation of such a mixture and lack of material. On continuing the elution with chloroform containing 15% ethanol, another component was recovered from the filtrate. This material had a specific rotation of −44.4°. It melted at 205° and a mixture with pure β-longilobine melted at the same temperature. Its analysis corresponded to the formula $C_{18}H_{25}O_6N$. Its infrared spectrum was identical with that of β-longilobine, except that there were a few additional absorptions which did not correspond to those of riddelliine and may be due to another component.

**The Alkaloids of *Senecio Parksii*.**—An examination of the infrared spectrum of the crude alkaloid from *Senecio parksii* showed that it was mainly composed of riddelliine, associated with some β-longilobine. The infrared spectrum was not changed in any way even after repeated crystallization of the product. There was an additional absorption at 1094 cm.$^{-1}$, which was not present in the spectra of riddelliine or β-longilobine and must be ascribed to a third component.

**The Alkaloids of *Senecio Vulgaris*.**—The infrared spectrum of the sample from *Senecio vulgaris*, made available to us by Dr. R. H. F. Manske, showed that it was mainly composed of α-longilobine with appreciable amounts of senecionine. The low value for carbon obtained by Manske suggests that β-longilobine or riddelliine may also be present. Because of the small amount of material at our disposal, no separation experiments were undertaken.

The authors are grateful to Dr. R. H. F. Manske for supplying a specimen of the alkaloid from

*Senecio vulgaris* and to Mrs. J. L. Johnson for determination and interpretation of infrared spectra.

## Experimental

**Extraction of the Alkaloids.**—The coarsely ground plant material (entire plant) was extracted with 95% ethanol in a Soxhlet for forty-eight hours. The alkaloidal fraction was isolated by the procedure described for riddelliine.[3b] The yield of the alkaloidal fraction, once crystallized from ethanol, is presented in Table II.

TABLE II

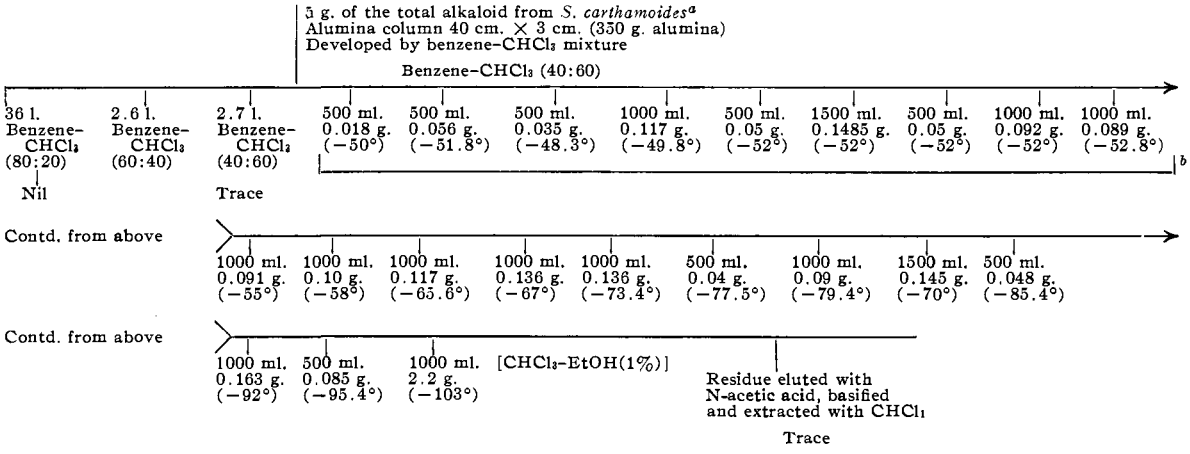
| Source | Yield, % |
|---|---|
| *S. douglasii* | 0.12 |
| *S. carthamoides* | .52 |
| *S. eremophilus* | .18 |
| *S. ampullaceus* | .025 |
| *S. parksii* | .19 |

filtrate, leaving β-longilobine and riddelliine on the alumina. The difficulties encountered in obtaining optically pure α-longilobine have been described in the introductory part under the discussion on the individual alkaloids from the several sources. In spite of numerous trials, no solvent or solvent combination could be discovered which would resolve senecionine and α-longilobine into widely separated zones on the adsorbent column. There was always an intermediate zone containing both these components. The process of isolation of the two components in a pure condition was therefore very tedious, involving repeated fractional chromatography.

Senecionine was isolated in appreciable amounts, from the total alkaloid of *Senecio carthamoides*, by developing and eluting with benzene–chloroform mixtures, with increasing proportions of chloroform as the chromatogram progressed. The procedure is illustrated in Table III. If the column was developed by chloroform alone, the recovery of pure senecionine from one operation was comparatively low. The steps involved in the isolation of the other alkaloids from the different sources

TABLE III

ISOLATION OF SENECIONINE FROM THE TOTAL ALKALOID OF *S. Carthamoides*




[a] Figures in parentheses indicate specific rotation. [b] These fractions were combined and recrystallized from ethanol, m. p. 238°. 0.0248 g. made up to 1 ml. in $CHCl_3$ gave $\alpha$ −1.32° at 28°; *l*, 1; $[\alpha]^{28}D$ −53.3°.

TABLE IV

| Source | M. p., °C. | $[\alpha]^{27}D$ ($CHCl_3$) | | Analyses, % C | H | N |
|---|---|---|---|---|---|---|
| *Senecio douglasii*[a] | 216–217 | −103 (5 rexl.) | Calcd. for $C_8H_{23}O_6N$ | 64.86 | 6.91 | 4.20 |
| | | | Found | 63.71 | 7.02 | 4.55 |
| | | −107 (17 rexl.) | Found | 64.50 | 7.39 | 4.34 |
| *Senecio carthamoides*[b] | 220–221 | −109 | Found | 64.82 | 7.54 | 4.28 |
| *Senecio eremophilus*[b] | 217–219 | − 94 | Found | 65.12 | 7.67 | 4.36 |
| *Senecio ampullaceus* | 212 | − 86 | Found | 64.76 | 7.30 | .. |
| *Senecio vulgaris*[2] | 222 | − 92.8 | Found | 63.04 | 7.20 | 4.26 |
| *Senecio parksii* | 210 | − 90 | Calcd. for $C_{18}H_{23}O_6N$ | 61.92 | 6.64 | 4.01 |
| | | | Found | 62.81 | 6.98 | 4.46 |

[a] Adams and Mueller, unpublished work. [b] Adams and Phillips, unpublished work.

**Separation of the Constituents of *Senecio Douglasii, Carthamoides, Eremophilus* and *Ampullaceus*.**—The alkaloids were introduced in chloroform solution onto the alumina columns without the preliminary treatment with alumina employed[1] in the case of the alkaloid from *Senecio longilobus*. The chromatographic fractionation procedure has been described at length in the previous communication.[1] All the alkaloids contained varying amounts of senecionine, which preceded the main α-longilobine fraction into the filtrate. By washing first with chloroform and then with chloroform containing 1% ethanol, senecionine and α-longilobine were eluted completely into the

are not presented due to considerations of space, but the relevant analytical data are summarized in Tables V–VIII.

The data on the alkaloids as extracted from the plants are given in Table IV.

**Hydrolysis of α- and β-Longilobine from the Different Sources.**—The hydrolysis was effected by the usual procedure[1] and the necine and necic acid portions were isolated. The melting points and analytical data of α- and β-longinecic acids

TABLE V

α-LONGILOBINE

| Source | M. p., °C. | M. p., °C. Mixtures[a] | [α]D | Found,[b] % C | H | N |
|---|---|---|---|---|---|---|
| *S. longilobus* | 217–218 | ... | −125.2 | 65.12 | 7.16 | 4.40 |
| *S. douglasii* | 217 | 217 | −125.2 | 64.79 | 7.03 | 4.23 |
| *S. carthamoides* | 215–216 | 215 | −115 | 64.96 | 7.00 | 4.44 |
| *S. eremophilus* | 215 | 215 | −101 | 64.40 | 7.39 | .. |
| *S. ampullaceus* | 217–218 | 217–218 | −100 | 64.91 | 7.17 | 4.41 |

[a] Melting points of mixtures with pure α-longilobine, from *Senecio longilobus*. All melting points are corrected. [b] Calcd. for $C_{18}H_{23}O_5N$: C, 64.86; H, 6.91; N, 4.20.

TABLE VI

α-LONGILOBINE METHIODIDE

| Source | M. p., °C. | M. p., °C. Mixtures[a] | Found,[b] % C | H | N |
|---|---|---|---|---|---|
| *S. longilobus* | 240 | ... | 47.92 | 5.64 | 3.17 |
| *S. douglasii* | 240 | 240 | 48.17 | 5.68 | 2.93 |
| *S. carthamoides* | 238 | 238 | 47.68 | 5.82 | .. |
| *S. eremophilus* | 236 | 236 | 48.48 | 5.73 | 3.09 |
| *S. ampullaceus* | 235 | 235 | 48.32 | 5.93 | 3.02 |

[a] Melting point of mixture with pure α-longilobine methiodide from *S. longilobus*. [b] Calcd. for $C_{18}H_{23}O_5N \cdot CH_3I$: C, 48.0; H, 5.48; N, 2.95.

TABLE VII

β-LONGILOBINE

| Source | M. p., °C. | M. p., °C. Mixtures[a] | [α]D | Found,[b] % C | H | N |
|---|---|---|---|---|---|---|
| *S. longilobus* | 207–208 | ..... | −49 | 61.61 | 7.35 | 4.12 |
| *S. douglasii* | 207–208 | 207–208 | −48.5 | 61.60 | 7.31 | 4.15 |
| *S. eremophilus* | 207–208 | 207–208 | −49.6 | 61.30 | 7.39 | 4.05 |
| *S. ampullaceus* | 205 | 205 | −44.4 | 61.93 | 7.53 | .. |

[a] Melting point of mixture with pure β-longilobine from *Senecio longilobus*. [b] Calcd. for $C_{18}H_{25}O_6N$: C, 61.5; H, 7.12; N, 3.98.

TABLE VIII

β-LONGILOBINE METHIODIDE

| Source | M. p., °C. | M. p., °C. Mixtures[a] | Found,[b] % C | H | N |
|---|---|---|---|---|---|
| *S. longilobus* | 256 | ... | 46.02 | 5.93 | 2.81 |
| *S. douglasii* | 256 | 256 | 46.44 | 5.89 | 2.72 |
| *S. eremophilus* | 256 | 256 | 46.34 | 5.71 | .. |
| *S. ampullaceus* | 254–256 | 254–256 | 46.67 | 5.76 | .. |

[a] Melting points of mixture with pure β-longilobine methiodide from *S. longilobus*. [b] Calcd. for $C_{18}H_{25}O_6N \cdot CH_3I$: C, 46.25; H, 5.68; N, 2.85.

TABLE IX

SENECIONINE

| Source | M. p., °C. | M. p., °C. Mixtures[a] | [α]D | Found,[c] % C | H | N |
|---|---|---|---|---|---|---|
| *S. carthamoides*[b] | 238 | 237–238 | −53.3 | 64.51 | 7.51 | 4.27 |
| *S. eremophilus* | 236 | 236 | −51.7 | 64.38 | 7.68 | |

[a] Melting point determination of mixture with authentic sample of senecionine from *S. cineraria*[4] (m. p. 236°). [b] The methiodide melted at 249°. Calcd. for $C_{18}H_{25}O_5N \cdot CH_3I$: C, 47.80; H, 5.91; N, 2.94. Found: C, 47.88; H, 6.10; N, 2.95. [c] Calcd. for $C_{18}H_{25}O_5N$: C, 64.48; H, 7.52; N, 4.17.

(4) Adams and Govindachari, THIS JOURNAL, 71, 1953 (1949).

obtained from the several sources are presented in Tables X and XI.

TABLE X

α-LONGINECIC ACID

| Source | M. p., °C. | M. p., °C. Mixtures[a] | Found,[c] % C | H |
|---|---|---|---|---|
| *S. longilobus* | 115 | ... | 56.16 | 6.34 |
| *S. douglasii* | 115 | 115 | 56.17 | 6.56 |
| *S. carthamoides* | 115 | 115 | 56.02 | 6.78 |
| *S. eremophilus*[b] | 117–118 | 116 | 56.20 | 7.18 |

[a] Melting point determination of mixture with pure α-longinecic acid from *S. longilobus*. [b] Infrared spectrum showed definite presence of senecic acid.[4] [c] Calcd. for $C_{10}H_{14}O_5$: C, 56.08; H, 6.54.

TABLE XI

β-LONGINECIC ACID

| Source | M. p., °C. | M. p., °C. Mixture[a] | Found,[b] % C | H |
|---|---|---|---|---|
| *S. longilobus* | 146 | ... | 51.68 | 7.00 |
| *S. douglasii* | 146 | 146 | 52.03 | 6.95 |
| *S. eremophilus* | 146 | 146 | 51.74 | 7.32 |

[a] Melting point determination of mixtures with pure β-longinecic acid from *S. longilobus*. [b] Calcd. for $C_{10}H_{16}O_6$: C, 51.8; H, 6.95.

**Hydrolysis of Senecionine from *S. carthamoides*.**—The hydrolysis was effected by the usual procedure and the dibasic senecic acid[4] was isolated, melting at 141°. This was converted to senecic acid lactone by the procedure previously described and submitted for analysis, m. p. 154°. Melting point of mixture with authentic sample of senecic acid lactone, 154°.

Calcd. for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.69; H, 7.21.

## Summary

The alkaloids isolated from *Senecio douglasii, carthamoides, eremophilus* and *ampullaceus* were mixtures which could not be separated into their pure components by fractional crystallization procedures. By employing a chromatographic fractionation procedure, with alumina as the adsorbent, these alkaloids have been shown to be mixtures of some or all of the four alkaloids, α-longilobine ($C_{18}H_{23}O_5N$), β-longilobine, ($C_{18}H_{25}O_6N$), senecionine ($C_{18}H_{25}O_5N$) and riddelliine ($C_{18}H_{23}O_6N$). The identity of the components has been established by actual isolation in optically pure condition and when this proved difficult, by infrared spectra. Further proof has been furnished by hydrolysis of these components to the corresponding necic acids and comparison with authentic specimens.

The alkaloid isolated by Manske from *Senecio vulgaris* is probably composed mainly of α-longilobine and senecionine, with some β-longilobine or riddelliine. The alkaloid isolated from *Senecio parksii* is probably a mixture of riddelliine and β-longilobine. The evidence in these two cases is based entirely on infrared spectra.

URBANA, ILLINOIS RECEIVED MARCH 25, 1949