456. *Alkaloids of New Zealand* Senecio *Species. Part II.*[1] *Senkirkine* *

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Re-investigation of the bases from *Senecio kirkii* Hook.f. has shown the presence of senkirkine,[1] *O*-acetylsenkirkine, and traces of two further alkaloids. Senkirkine is identical with renardine,[2,3] from *S. renardi* C. Winkl. Chemical and physical evidence supports the structure (II; R = H) deduced for renardine from *X*-ray crystallographic analysis of retusamine,[4] a related alkaloid from *Crotalaria retusa* L.[5]

In an earlier investigation [1] the isolation of a new alkaloid, senkirkine ($C_{18}H_{25}NO_6$), from *Senecio kirkii* Hook.f. was described. Alkaline hydrolysis afforded senecic acid lactone and a liquid necine from which only an amorphous picrate and aurichloride were obtained.

It has now been found that all parts of the plant contain alkaloids, with the greatest quantity in the leaves from which they are best extracted with cold aqueous acetic acid. Paper chromatography indicated the presence of four alkaloids, A, B, C, and D, which were separated on a larger scale by Culvenor, Drummond, and Price's method [6] utilising partition techniques. Alkaloid B was identified as senkirkine, and alkaloid D as *O*-acetylsenkirkine, obtained by acetylation of senkirkine. Alkaloids A and C were obtained in trace amounts only, precluding a detailed investigation.

Further analyses of senkirkine and its derivatives as well as the integrated n.m.r. spectrum of the parent base now support the formula, $C_{19}H_{27}NO_6$, and from the infrared spectrum (see later) it appears to be a cyclic diester typical of other alkaloids from *Senecio* species.[7] Senkirkine undergoes extensive decomposition at temperatures above the melting point, and attempted determination of the mass spectrum gave no peak corresponding to the molecular ion. Acid and alkaline hydrolyses again afforded senecic acid or its lactone and a liquid necine which formed a crystalline, hygroscopic hydrochloride, m. p. 145—147°, but for which satisfactory analyses were not obtained. However, assuming normal hydrolysis, the necine should have the formula, $C_9H_{15}NO_3$, according to the equation:

$$C_{19}H_{27}NO_6 + 2H_2O \longrightarrow C_{10}H_{16}O_5 + C_9H_{15}NO_3$$

* Presented in part to an International Conference on Phytochemistry and Medicinal Plants of the Pacific Area in Noumea, New Caledonia, May 1964.

[1] Part I, L. H. Briggs, J. L. Mangan, and W. E. Russell, *J.*, 1948, 1891.
[2] A. V. Danilova and R. A. Konovalova, *Zhur. obshchei Khim.*, 1950, **20**, 1921.
[3] A. V. Danilova, N. I. Koretskaya, and L. M. Utkin, *Zhur. obshchei Khim.*, 1961, **31**, 3815.
[4] J. A. Wunderlich, *Chem. and Ind.*, 1962, 2089.
[5] C. C. J. Culvenor and L. W. Smith, *Austral. J. Chem.*, 1957, **10**, 464.
[6] C. C. J. Culvenor, L. J. Drummond, and J. R. Price, *Austral. J. Chem.*, 1954, **7**, 277.
[7] For reviews on *Senecio* alkaloids see F. L. Warren, *Fortschr. Chem. org. Naturstoffe*, 1955, **12**, 198; N. J. Leonard in " The Alkaloids," Academic Press, New York, 1960, vol. 6.

Hydrogenolysis followed by hydrolysis gave a reduced liquid necine, $C_9H_{17}NO_2$, characterised as its picrate, m. p. 219—220°.

Senkirkine contains three *C*-Me groups (Kuhn–Roth and n.m.r. spectrum), which are accommodated in the senecic acid portion and, from a Herzig–Meyer determination, the n.m.r. spectrum, and a band in the infrared spectrum (LiF optics) at 2800 cm.$^{-1}$,[8] an *N*-methyl group. Failure to form a nitrosamine and the formation of a methiodide indicates that the nitrogen is tertiary, while the *N*-methyl group precludes the usual 4-methylpyrrolizidine type of necine.

Senkirkine inexplicably exhibits only one band in the normal carbonyl region in chloroform (at 1730 cm.$^{-1}$) or in carbon tetrachloride (at 1739 cm.$^{-1}$) solution but shows two in a potassium bromide disc, at 1715 and 1739 cm.$^{-1}$, assigned to αβ-unsaturated and saturated ester groups, respectively. Since senkirkine is thus the usual cyclic diester two of the oxygen atoms in the necine must have alcoholic functions, leaving one oxygen atom unassigned. *O*-Acetylsenkirkine exhibits no free hydroxyl band in the infrared spectrum and since the hydroxyl group acetylated is that in the senecic acid moiety the remaining oxygen atom in the necine cannot be hydroxylic.

No band typical of a normal carbonyl group appears in the remaining infrared spectrum of senkirkine or in that of the necine hydrochloride. Senkirkine also fails to react with normal carbonyl reagents. From the n.m.r. spectrum carried out with the addition of deuterium oxide only the hydroxylic proton in senkirkine undergoes exchange while no exchange occurs in *O*-acetylsenkirkine.

Measurement of the pK_b of senkirkine, 7·64, showed that it is a relatively weak base reminiscent of solasodine [9] and indicated the possible effect of the remaining oxygen atom on the nitrogen atom.

The above properties and a comparison of the melting points of their respective derivatives indicated that senkirkine is identical with renardine, $C_{19}H_{27}NO_6$, from *S. renardi* C. Winkl,[2,3] and from *Nardosmia laevigata*.[10]

	Senkirkine	Renardine
Free base	m. p. 196·5—197·5°	m. p. 197—197·5
	$[\alpha]_D^{20}$ −16°	$[\alpha]_D^{20}$ −13°
Picrate	m. p. 222—223°	m. p. 219—220°
Bitartrate	m. p. 196·5—197·5°	m. p. 193—194°
Methiodide	m. p. 192—194° (decomp.)	m. p. 194—196° (decomp.)
Necine hydrochloride	m. p. 145—147°	m. p. 143°

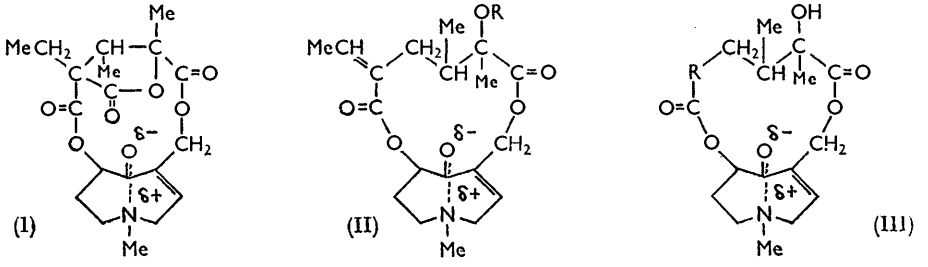
Indeed, direct comparison (mixed melting point and infrared spectra) of senkirkine with a sample of renardine, kindly provided by Mme. N. Koretskaya, confirmed their identity.

It has been established [2] that otonecine, the necine from otosenine [11] (identical with tomentosine [12]) is identical with that from the alkaloids renardine and onetine [13] and is probably identical with that from retusamine, a minor alkaloid from *Crotalaria retusa* L.[5] Otonecine possesses a potential carbonyl group [2,11] but no structure had been suggested by the Russian workers. From a recent *X*-ray diffraction analysis [4] of its α′-bromo-(+)-camphor-*trans*-π-sulphonate monohydrate Wunderlich has shown that retusamine has the structure (I), and, following a consideration of the infrared and other properties, has suggested the structures (II; R = H), (III; R = >C(O)—CHMe), and III; R = >C(OH)·C(OH)Me) for renardine, otosenine, and onetine, respectively.

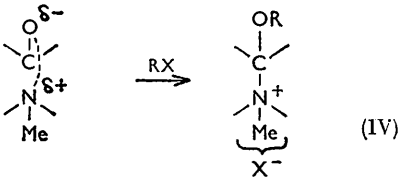
The chemical and physical properties of senkirkine completely support the structure suggested for renardine. A strong sharp band in the infrared spectrum at 1623 cm.$^{-1}$ can

[8] R. H. Hill and G. D. Meakins, *J.*, 1958, 760.
[9] H. Bloom and L. H. Briggs, *J.*, 1952, 3591.
[10] P. S. Massagetov and A. D. Kuzovkov, *Zhur. obshchei Khim.*, 1953, **23**, 158.
[11] E. S. Zhdanovich and G. P. Men'shikov, *Zhur. obshchei Khim.*, 1941, **11**, 835.
[12] H. B. Schröter and F. Šantavý, *Coll. Czech. Chem. Comm.*, 1960, **25**, 472; F. Šantavý, *Planta Medica*, 1958, **6**, 78.
[13] A. V. Danilova, N. I. Koretskaya, and L. M. Utkin, *Zhur. obshchei Khim.*, 1962, **32**, 647.

be assigned to the C ⋯ $O^{\delta-}$ stretching since this varies with the medium, occurring at 1618 cm.$^{-1}$ in chloroform and at 1656 cm.$^{-1}$ in carbon tetrachloride, while the remaining weak band in the 1500—1600 cm.$^{-1}$ region at 1667 cm.$^{-1}$ remains constant.* The C ⋯ $O^{\delta-}$ stretching band is absent in the infrared spectra of the salts of senkirkine and also in that



of the necine hydrochloride due to the protonation of the carbonyl oxygen atom as indicated (IV; R = H). The low pK_b value for senkirkine is also typical of azacyclic ketones exhibiting transannular interaction.[15]



The n.m.r. spectrum of senkirkine (Figure) is particularly enlightening; not only does it agree with the suggested formula but, in conjunction with spin–spin decoupling experiments, it enables an assignment to be made for all twenty-seven protons. In the following discussion the peaks are numbered from lower to higher field according to the protons in the suggested structure (V) which give rise to them.

A one-proton triplet at δ 6·18 is assigned to the vinyl proton (1) coupled with two adjacent methylene protons (a corresponding proton in the spectrum of the related alkaloid jacozine gives rise to a poorly resolved triplet at δ 6·25 [16]). A quartet centred at δ 5·92, arising from the single proton (2), is due to coupling (J = 8 c./sec.) to the adjacent methyl group (12). It shows further allylic coupling ($J \approx 1$ c./sec.) to one of the protons of the methylene group (10). The methylene protons (3) and (5) are non-equivalent and give rise to two doublets (J = 12 c./sec.) at δ 5·46 and 4·37, respectively (similar doublets at δ 5·50 and 4·10 with coupling constants of 12 c./sec. appear in the spectrum of jacozine). Spin–spin decoupling experiments showed that proton (1) is weakly coupled to proton (5). A one-proton triplet at δ 5·03, associated with proton (4), arises from coupling with the adjacent methylene group (9) and its position is consistent with the literature value (δ 5·01) [17] for the system >CH·O·CO·alkyl. A two-proton peak at δ 3·37 is assigned to the methylene protons (6) since its broadening and position suggest nitrogen interaction.[17] The assignment of a sharp one-proton singlet at δ 3·2 to the hydroxyl group (7) was confirmed by its disappearance on equilibration with deuterium oxide (Figure). From spin–spin decoupling experiments it was possible to assign three two-proton multiplets, centred at

* Cf. The infrared spectrum of 1-methyl-2-pyridone in various solvents where a similar lowering of the carbonyl frequency occurs,[14] a frequency which also changes with the solvent.

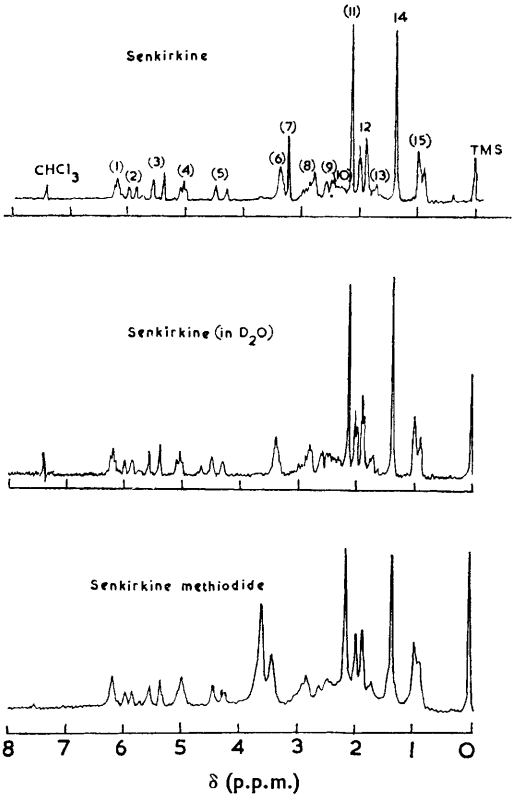
[14] L. J. Bellamy and P. E. Rogasch, *Spectrochim. Acta*, 1960, **16**, 30; A. R. Katritzky and R. A. Jones, *J.*, 1960, 2947.

[15] N. J. Leonard, *Record Chem. Progress*, 1956, **17**, 243.

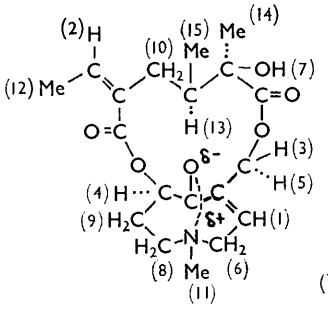
[16] C. C. J. Culvenor, *Austral. J. Chem.*, 1964, **17**, 233.

[17] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

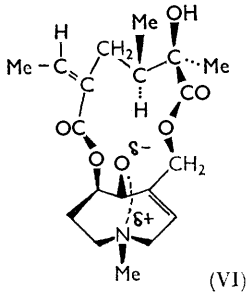
approximately δ 2·8, 2·5, and 2·3, to the methylene groups (8), (9), and (10), respectively. Protons (9) at δ 2·5 were coupled to proton (4), and protons (10) at δ 2·3 were coupled to proton (2). Assignment of protons (8) to the peak at δ 2·8 then followed by elimination.



A three-proton singlet at δ 2·11 is assigned to the *N*-methyl group (11) (cf. δ 2·20 [17]). A doublet at δ 1·90, with a coupling constant (8 c./sec.) consistent with literature values [17] and assigned to the methyl group (12), showed further splitting by homoallylic coupling [18] ($J \simeq 1{\cdot}5$ c./sec.) to one of the protons of the methylene group (10).* The secondary methyl



(V)



(VI)

group (15) gives rise to a three-proton doublet at δ 0·90 from coupling (J = 6·5 c./sec.) with the adjacent proton (13), and the latter in turn appears as a one-proton multiplet centred at

* The corresponding doublets at δ 1·27 and 1·25 in the spectra of jacozine and jacobine respectively occur at lower field as a result of their proximity to the strong deshielding influence of the epoxide ring.[16]

[18] J. T. Pinhey and S. Sternhell, *Tetrahedron Letters*, 1963, No. 4, 275.

δ 1·68 as a result of additional coupling to the protons of the methylene group (10). Assignment of a three-proton singlet at δ 1·33 to the methyl group (14) follows from the fact that it is the only tertiary C methyl group in the molecule.

The integrated (29 protons) n.m.r. spectrum of *O*-acetylsenkirkine (II; R = Ac) is similar to that of the parent base, differing mainly in the fact that the hydroxyl peak is replaced by a three-proton singlet at δ 3·23. As expected, the tertiary methyl group, corresponding to (14) in the parent compound, shows a marked downfield shift to δ 1·71 as a result of the deshielding influence of the acetyl group.

On the basis of formula (II; R = H) for senkirkine, its methiodide should have the partial structure (IV; R = Me; X = I). In accord with this, its integrated n.m.r. spectrum (30 protons) is similar to that of senkirkine, with the addition of a broad singlet at δ 3·61 corresponding to four protons. Three of these protons are assigned to an *O*-methyl group and the fourth to the hydroxyl group of the necic acid portion.

From the configurational assignments of Nair and Adams,[19] and of Masamune,[20] the *X*-ray structural determination of jacobine,[21] and the recent correlation of the asymmetric centres of epoxyjaconecic and senecic acids,[22] the relative and absolute configuration of the latter is known. Although no direct comparison of otonecine with the necine of retusamine has been made, it appears highly probable that the compounds are identical. Hence, combining the structure of otonecine with senecic acid leads to the formulation (VI) as representing the probable absolute configuration of senkirkine.

Experimental

Analyses were by Dr. A. D. Campbell and his associates, University of Otago. Ultraviolet spectra were measured for ethanol solutions with a Perkin-Elmer model 137 u.v. spectrophotometer and infrared spectra, unless otherwise stated, for potassium bromide discs with a Perkin-Elmer Infracord spectrophotometer. Nuclear magnetic resonance spectra were measured in deuterochloroform with a Varian A-60 spectrometer using tetramethylsilane as internal reference. Spin–spin decoupling experiments were carried out with a Varian HR-60 spectrometer. Whatman No. 1 paper was used for chromatography.

Extraction of Alkaloids.—Small-scale extraction of various parts of the plant (dried and fresh) with methanol (Soxhlet), cold 1% acetic acid (with or without continuous stirring) were followed by measurement of the total alkaloid content in aliquot parts by precipitation with silicotungstic acid. Extractions by Koekemoer and Warren's method [23] indicated the absence of amine oxides.

In a typical extraction, fresh milled leaves (40 kg.) collected from the Waitakere Ranges, Auckland, in February, were soaked in 1% acetic acid for 4 days and filtered through muslin and then in the normal way. Basification of the extract with ammonia precipitated a brown solid which was almost devoid of alkaloid and was filtered off. The filtrate was then extracted with chloroform to yield a clear brown gum. A cleaner and partly crystalline product could be obtained by extracting the chloroform solution with dilute acetic acid and completing the process.

Descending paper chromatography was carried out by using the upper phase from shaking equal volumes of n-butanol and 5% acetic acid, the paper being allowed to equilibrate with the lower phase for 24 hr. Four alkaloids, A, B, C, and D, were detected (dilute Dragendorff's reagent) with R_F values of 0·45, 0·59, 0·66, and 0·76, respectively, with A, C, and D in minor amounts only.

By using Culvenor, Drummond, and Price's method [5] the crude bases were separated on a partition column of Celite moistened with N-sodium dihydrogen phosphate and developed with chloroform–carbon tetrachloride mixtures and then chloroform. Fractions were automatically collected and the progress of separation was followed by paper chromatography.

[19] M. D. Nair and R. Adams, *J. Amer. Chem. Soc.*, 1960, **82**, 3786; 1961, **83**, 922.
[20] S. Masamune, *J. Amer. Chem. Soc.*, 1960, **82**, 5253.
[21] J. Fridrichsons, A. McL. Mathieson, and D. J. Sutor, *Tetrahedron Letters*, 1960, No. 23, 35.
[22] N. I. Koretskaya, A. V. Danilova, and L. M. Utkin, *Zhur. obshchei Khim.*, 1962, **32**, 3823; see also ref. **16**.
[23] M. J. Koekomoer and F. L. Warren, *J.*, 1951, 66.

Alkaloid D (O-*Acetylsenkirkine*).—Alkaloid D, eluted from the column with carbon tetrachloride–chloroform (9 : 1), crystallised from ethyl acetate as short needles, m. p. 202—203° (decomp.). Recrystallisation from ethyl acetate–acetone afforded *needles* (25 mg.; 0·005%), m. p. 195—196°, $[\alpha]_D^{23}$ −34° ± 1° (*c.* 0·44 in MeOH), which were found to be hygroscopic after being dried for analysis (Found: C, 53·9; H, 7·7; N, 3·1; *N*-Me, 2·75. $C_{21}H_{29}NO_7 \cdot 3H_2O$ requires C, 54·6; H, 7·6; N, 3·0; *N*-Me, 3·3%); $\lambda_{max.}$ 218 mμ (log ε 3·81); $\nu_{max.}$ 1761 (OAc), 1739 (ester CO), 1727 (conj. ester CO), 1689 (C:C), 1639 (C⋯O$^{\delta-}$), 1241 cm.$^{-1}$ (OAc).

The *picrate* crystallised from aqueous ethanol as plates, m. p. 208—209° (Found: C, 51·3, 51·4; H, 5·3, 5·3; N, 8·5. $C_{21}H_{29}NO_7,C_6H_3N_3O_7$ requires C, 51·6; H, 5·1; N, 8·9%). The *picrolonate* crystallised from aqueous methanol as needles, m. p. 222° (Found: C, 55·1; H, 5·9; N, 10·3. $C_{21}H_{29}NO_7,C_{10}H_8N_4O_5$ requires C, 55·4; H, 5·55; N, 10·4%). The *aurichloride* crystallised from aqueous ethanol as yellow needles, m. p. 108—109° (Found: *M*, 766. $C_{21}H_{29}NO_7,HAuCl_4$ requires *M*, 747).

Hydrolysis of alkaloid D with barium hydroxide as for senkirkine (see later) gave a brown oil containing a necine, R_F 0·28, identical with that from senkirkine.

Senkirkine.—Fractions eluted from the column with carbon tetrachloride–chloroform (4 : 1) afforded senkirkine (alkaloid B) (0·04—0·1%), which crystallised from ethyl acetate or acetone as bevelled plates, m. p. 196·5—197·5°. Further senkirkine was isolated from the mother-liquors as the bitartrate (cf. ref. 2), $[\alpha]_D^{25}$ −16° ± 1° (*c* 1·89 in MeOH), $[\alpha]_D^{23}$ −19° ± 1° (*c* 1·33 in EtOH) (Found: C, 62·4, 62·5, 62·6; H, 7·4, 7·4, 7·2; N, 4·1, 4·0, 3·85; CMe, 10·5; NMe, 3·7; OMe, nil. $C_{19}H_{27}NO_6$ requires C, 62·45; H, 7·45; N, 3·8; 3CMe, 12·3; NMe 4·1%); $\lambda_{max.}$ 219 mμ (log ε 4·02); $\nu_{max.}$ 3424 (OH), 1739 (ester CO), 1715 (conj. ester CO), 1656 (C:C), 1618 (C⋯O$^{\delta-}$), 1362 and 1166 cm.$^{-1}$ (tert. OH), $\nu_{max.}$ (LiF optics) 2800 cm.$^{-1}$ (NMe). The m. p. was undepressed by a sample of renardine, m. p. 195·5—196·5°, and the infrared spectra were identical. Potentiometric titration [9] gave pK_b 7·64. Senkirkine gave a positive pine splint test [24] (cf. ref. 2) and failed to give a 2,4-dinitrophenylhydrazone or oxime under normal conditions.

Alkaloids A and C.—From the fractions with R_F 0·66 a small quantity (13 mg.) of alkaloid C was obtained as colourless microscopic needles, m. p. 210·5—212·5° (decomp.), for which a satisfactory analysis was not obtained. It contained an *N* Me group (Found: 3·1%) and had $\lambda_{max.}$ 215 mμ ($E^{1\%}$ 490), and formed a picrate, needles, m. p. 224—225°, from methanol.

Only a trace of the material with R_F 0·45 could be obtained from the appropriate fractions eluted with chloroform, insufficient for further investigation.

Salts of Senkirkine.—The following salts of senkirkine were prepared: *Picrate*, yellow rods from aqueous ethanol, m. p. 225—225·5° (Found: C, 51·2; H, 4·9; N, 9·7. $C_{19}H_{27}NO_6$, $C_6H_3N_3O_7$ requires C, 52·0; H, 5·2; N, 9·7%). *Picrolonate*, orange-yellow needles from water, m. p. 138° (Found: C, 54·1; H, 6·1; N, 12·2. $C_{19}H_{27}NO_6,C_{10}H_8N_4O_5$ requires, C, 53·7; H, 5·5; N, 11·6%). *Aurichloride*, yellow flakes from aqueous ethanol, m. p. 182·5—183·5° (Found: *M*, 721. $C_{19}H_{27}NO_6,HAuCl_4$ requires *M*, 705). *Chloroplatinate*, orange needles from aqueous ethanol, decomposing at 196—197° (Found: C, 40·4, 40·7; H, 5·2, 5·0; Pt, 17·0. $C_{19}H_{27}NO_6$, H_2PtCl_6 requires C, 40·0; H, 4·95; Pt, 17·1%). *Bitartrate*, colourless plates from ethanol, m. p. 196·5—197·5° (Found: C, 53·6; H, 6·8. $C_{19}H_{27}NO_6,C_4H_6O_6$ requires, C, 53·6; H, 6·4%). *Methiodide*, colourless needles from acetone–ether, decomposing at 192—194° (Found: N, 3·5. $C_{20}H_{30}INO_6$ requires N, 2·8%).

Senkirkine also formed a 2,4-*dinitrobenzenesulphonyl chloride*, m. p. 189—190°, and a *reineckate*, m. p. 169·5—170·5°.

O-*Acetylsenkirkine.*—Senkirkine (100 mg.) was heated under reflux with acetyl chloride (0·2 c.c.) and the excess of reagent removed *in vacuo*. Trituration of the resulting gum with acetone and then ethyl acetate gave a solid which afforded *O*-acetylsenkirkine (56 mg.), m. p. 195·5—196·5°, identical with alkaloid D by mixed m. p., R_F value on co-chromatography, and infrared spectra. The derivative was hygroscopic after being dried for analysis (Found: C, 57·1, 57·1; H. 7·5, 7·3; N, 3·2. Calc. for $C_{21}H_{29}NO_7,2H_2O$: C, 56·9; H, 7·5; N, 3·2%).

The picrate had m. p. 210—211°, undepressed by the picrate of alkaloid D (Found: C, 51·2; H, 5·5; N, 8·7. Calc. for $C_{21}H_{29}NO_7,C_6H_3N_3O_7$: C, 51·6; H, 5·1; N, 8·9%). Attempts to acetylate senkirkine with acetic anhydride–pyridine at 20° were unsuccessful while reaction under reflux resulted in decomposition.

[24] E. Erdmann and H. Erdmann, *Ber.*, 1899, **32**, 1213.

Hydrolysis of Senkirkine.—(*a*) *With alkali.* Alkaline hydrolysis by Liesegang and Warren's procedure [25] produced the necine as a brown oil, R_F 0·28, from which only an amorphous picrate, m. p. 170—180° (decomp.), could be obtained (cf. refs. 1 and 2). From the acid fraction a product was obtained which, after treatment with concentrated hydrochloric acid and evaporation at 100°, afforded senecic acid lactone, colourless needles from ethyl acetate, m. p. and mixed m. p. 155—156°, $[\alpha]_D^{23}$ +42° (*c* 0·295 in EtOH) (Found: C, 60·7; H, 7·0. Calc. for $C_{10}H_{14}O_4$: C, 60·6; H, 7·1%). $\lambda_{max.}$ 225 mμ (log ε 3·63) (identical infrared spectrum).

(*b*) *With acid.* Senkirkine (1 g.) was heated with 10% hydrochloric acid (5 c.c.) at 100° for 40 hr. Continuous ether extraction of the product afforded, after lactonisation, senecic acid lactone, m. p. 155—156° (yield 90%). If the lactonisation step was omitted senecic acid was obtained, colourless needles (from acetone), m. p. 144—145°; $\lambda_{max.}$ 215 mμ (log ε 3·79). Attempts to acetylate senecic acid with acetic anhydride–pyridine under reflux were unsuccessful.

The remaining acid solution on evaporation to dryness in a desiccator formed the necine hydrochloride as a gum (200 mg.) which crystallised when triturated with acetone. It was also obtained crystalline by chromatography on Whatman No. 3MM paper, developing with butan-1-ol saturated with 5% acetic acid, and extracting the major band with methanol. The hydrochloride, m. p. 145—147°, $[\alpha]_D^{23}$ −13° ± 1° (*c* 0·96 in EtOH) (Danilova *et al.*[2] record m. p. 143° for otonecine hydrochloride; Zhdanovich and Menshikov [11] record m. p. 146—148°), was very hygroscopic and could not be recrystallised. The infrared spectrum (KBr) had bands at 3378, 3148 (OH), 1657 (C:C), but none in the carbonyl region.

Hydrogenation.—By the employment of palladium–barium sulphate catalyst [26] 1·72 moles of hydrogen per mole were absorbed in 65 min., the first mole in 10 min.

Hydrogenation of senkirkine (100 mg.) on a larger scale gave a mixture of products, R_F's 0·72 (major spot) and 0·38, from which no pure alkaloid or crystalline derivative could be isolated.

Hydrogenolysis.—With Adams platinum oxide catalyst 3 moles of hydrogen per mole were absorbed in 30 min. followed by gradual uptake of hydrogen (0·7 mole).

Hydrogenolysis of senkirkine (1·0 g.) with Adams catalyst (70 mg.) for 55 hr., followed by hydrolysis and working up in the usual manner gave a gum containing three substances, R_F's 0·36 (major spot), 0·53, and 0·68. The substance, R_F 0·36, was isolated as a gum by chromatography on cellulose packed as a slurry with the organic phase of a mixture of n-butanol–5% acetic acid, and developed with n-butanol. It had $\nu_{max.}$ 3257 cm.$^{-1}$ (OH) (no carbonyl or double bond absorption) and formed a *picrate*, m. p. 219—220° (decomp.) (from propyl acetate) (Found: C, 45·5; H, 5·1; O, 35·9; N, 13·6. $C_9H_{17}NO_2,C_6H_3N_3O_7$ requires C, 45·0; H, 5·0; O, 36·0; N, 14·0%).

We are greatly indebted to Dr. J. N. Shoolery for the earlier measurements of n.m.r. spectra, to Dr. R. M. Golding for the spin–spin decoupling experiments, and to Drs. A. L. G. Rees and A. J. C. Nicholson for the mass spectrum experiments. Grateful acknowledgment is made to the Chemical Society, the Rockefeller Foundation of New York, the Australian and New Zealand Association for the Advancement of Science, and the Research Committee of the New Zealand Universities Grants Committee for grants.

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Auckland, New Zealand. [*Received, June 15th,* 1964.]

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