Noakes (1963) consider that there may be a second-order phase transition to the low temperature form. A slight shift in the alignment of the azide ions is the most obvious difference which could occur.

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An X-ray Examination of the Chloroplatinate of an Alkaloid derived from *Senecio kirkii*

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The chloroplatinate of an alkaloid believed to be senkirkine has been studied by three-dimensional X-ray methods, and its structure determined. The cation has the formula $[C_{18}H_{28}NO_6]^+$, and differs in the absence of a methylene group from that corresponding to the now known structure of senkirkine. The relationship of the two alkaloids is not known.

Introduction

The alkaloid senkirkine was first isolated from the shrub *Senecio kirkii* Hook. f. by Briggs, Mangan & Russell (1948), who ascribed to it the formula $C_{18}H_{25}NO_6$. Hydrolysis gave a lactone which was identified as that of senecic acid, $C_{10}H_{16}O_5$, but no definite information was obtained concerning the necine base. More recent investigations by Briggs, Cambie, Candy, O'Donovan, Russell & Seelye (1965) suggested a revised formula $C_{19}H_{27}NO_6$ and elucidated various features of the base, but difficulty in establishing both its structure and its mode of attachment to the necic acid led to an investigation of the crystal structure of a derivative of the alkaloid. Crystals were prepared which were thought to be the chloroplatinate of senkirkine, and the structure determination of these crystals is herein described.

In the interim the structure of senkirkine has been established by other means (Briggs *et al.*, 1965) and it appears that the compound studied is not the salt of senkirkine but that of a closely related alkaloid.

Experimental

Light-orange crystals were obtained by mixing aqueous solutions of chloroplatinic acid and what was considered to be a pure sample of senkirkine. The molecular weight from the crystal data was as expected, and no further precautions were taken to ensure the identity of the crystals.

Small equant crystals were used for X-ray photographs. Where necessary, larger crystals were cut to size with the use of the solvent saw technique described by Peterson, Steinrauf & Jensen (1960). Immediately following their preparation crystals could be obtained which gave excellent photographs and were able to withstand many hours of X-radiation without signs of decomposition. After some weeks the crystals began to deteriorate, and proved far more sensitive to X-rays. It proved necessary to use a number of crystals to complete the data collection, and those used in the later stages would not have been considered acceptable at the beginning. An attempt at recrystallization of the limited material available gave crystals with different cell dimensions.

The crystal data were as follows:

Monoclinic
$a=13{\cdot}72\pm0{\cdot}03$, $b=9{\cdot}90\pm0{\cdot}03$, $c=18{\cdot}91\pm0{\cdot}04$ Å; $\beta=95{\cdot}60\pm0{\cdot}20°$.
$D_m=1{\cdot}55$ g.cm^{-3}.
D_c, for formula $(C_{18}H_{28}O_6N)_2PtCl_6 . 2H_2O$, $Z=2$, $=1{\cdot}543$ g.cm^{-3}.
Systematic absences: Reflexions hkl absent when $h+k$ odd.
Space group: $C2$. *Senecio* alkaloids are optically active, and hence the mirror-image operation cannot exist.

Determination of the structure

By symmetry the platinum atoms lie on the diad axis, and a direct Fourier synthesis could be calculated for the (010) projection. The chlorine atoms of the chloroplatinate ion were clearly defined, but the light atoms are poorly resolved in this projection (Fig. 1) and interpretation was not possible.

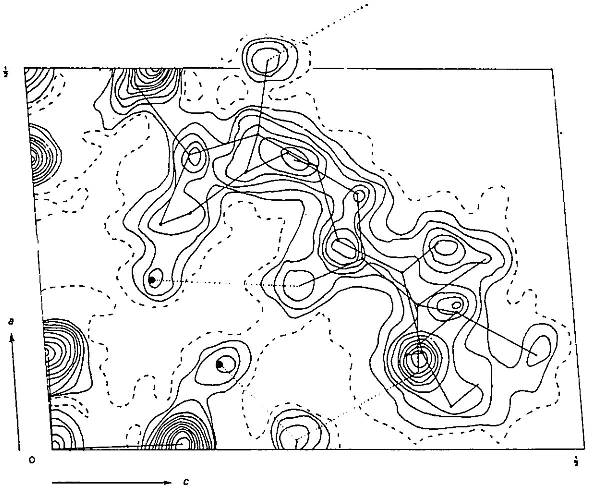
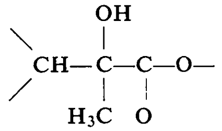


Fig. 1. The electron density projection on (010). The molecule is outlined, and the water molecules are indicated by solid circles. Intermolecular hydrogen bonds are indicated by dotted lines. The dashed contour is at 2 e.Å^{-2}, and full contours (other than about the platinum atom) are at intervals of 2 e.Å^{-2}.

The platinum atom was assumed to define the origin in the y direction, and y coordinates could be allocated to the chlorine atoms by assuming the $PtCl_6^{2-}$ ion to be regularly octahedral. A three-dimensional Fourier synthesis was then calculated, with phases given by the heavy atoms. Terms were not included where $\sin\theta>0{\cdot}85$, and where $F_o+F_H<\frac{1}{6}F_L$, where F_o is the observed amplitude, F_H the amplitude of the chloroplatinate contribution to the structure factor, and F_L the maximum contribution of the light atoms. (The platinum contributes to all terms, and F_H was always large.) Over and above the heavy atoms, 33 distinct maxima appeared with $\varrho_{\max}$ greater than 4 e.Å^{-3}. A diffraction ripple of height 10 e.Å^3 surrounded the platinum atom at a radius of 1·5 Å, and a number of smaller maxima occurred along symmetry lines such as $y=z=0$. These were abnormally sharp and were thought to be spurious. Because the heavy atoms comprise a centrosymmetric group the synthesis possesses a false mirror plane at $y=0$, and the problem was essentially to extricate the molecule from its superposed image. The successful analysis began when a grouping of peaks was identified with the heavy atoms of the arrangement



which was known to exist in the necic acid. Only one such grouping could be found, and it proved possible to trace from it the whole of the acid sequence, with each atom selected satisfying the expected requirements of bond length and angle. The carboxyl group originally identified was connected, *via* the expected methylene carbon, to a clearly defined five-membered ring. The other carboxyl was connected, again *via* one further atom, to an adjacent atom of the same five-membered ring. Detailed interpretation of the substituents of this ring was not attempted. All of the 27 light atoms were represented among the 33 peaks in the synthesis, and 25 were recognized at this stage. Of these, 23 were included in the first structure factor calculation. The water molecule O(7) was clearly defined, but as it had no connection with the remainder of the molecule it was omitted, as was atom C(13). It is this atom which defines the acid as senecic and not its geometric isomer intergerrenecic acid, and it was thought desirable to have further confirmation of its existence. The four oxygen atoms in the ester linkages were calculated as such, and all other light atoms given carbon scattering factors. Values of 2·0, 4·0 and 6·0 were assumed for the platinum, chlorine and light atom temperature factors. (The Wilson plot value for the temperature factor was 5·8.) A second Fourier synthesis was then calculated. The peaks corresponding to the light atoms included were enhanced, and with one exception their images were effectively removed. Atom C(4) had been included with coordinates (0·38, −0·21, 0·25). The peak which occurred was markedly elongated, in the y direction, and had its maximum at (0·38, −0·225, 0·25). A residual peak ($\varrho_{\max}=4{\cdot}2$ e.Å^{-3}) appeared also in the image position with maximum at (0·38, 0·255, 0·245). Reference to the original heavy atom phased synthesis showed that the peak which had been interpreted as C(4) was considerably elongated in the [010] direction and of sufficient volume to represent two atoms, with y coordinates approximately $\pm 0{\cdot}21$ and $\pm 0{\cdot}29$. From consideration of bond lengths it was apparent that these were C(16) and C(4) with y coordinates $+0{\cdot}21$ and $-0{\cdot}29$ respectively. The only other major peaks in the heavy atom synthesis which had not been included as atoms and which had persisted convincingly were assigned to C(13), O(7) and O(8). The false images of the former two were still present, the density at the correct site being slightly enhanced. The remaining peaks of the original synthesis were either substantially diminished or obviously spurious. No reason was ever found to doubt the interpretation made at this stage, which was as in Fig. 2, with two additional atoms, O(7) and O(8), not connected to the molecule but with environment consistent with their being molecules of water of crystallisation. The assignment of the nitrogen atom and of C(18) as a methyl group followed from the assumption that the base was derived from a methylpyrrolizidine nucleus, and, following infrared spectral evidence, that the nitrogen was connected to a methyl group. Atom O(6), assumed to be carbon in the structure factor calculation, appeared as one of the largest peaks in the subsequent Fourier synthesis (integrated peak value 7·8 electrons) and was thus assigned as a hydroxyl group. The allocation of O(3) rather than C(7) as a hydroxyl group was equally obvious. The water molecule O(7) lay very close to the false mirror plane and was assumed to have zero y coordinate. The water molecule O(8) made an approach of 2·5 Å to C(18) if its y coordinate were positive, and a similar approach to O(6) if it were negative. The choice of the latter was thus dependent on the above assignment of atoms O(6) and C(18) but there was never reason to doubt it. Structure factors were then recalculated, giving an R index of 0·16 for the 2114 observed reflexions.

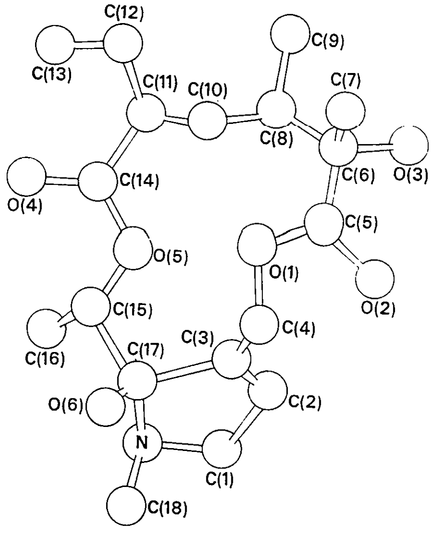


Fig. 2 The alkaloid cation.

At this stage of the work facilities were not available for further three-dimensional calculations, and the structure as deduced was refined *via* projections. The structure factor calculations were repeated, making correction for dispersion in the scattering of the platinum atom (Dauben & Templeton, 1955), and with an appropriate adjustment in the temperature factor. (Scattering curves used were those of Thomas & Umeda (1957) for platinum, of Tomiie & Stam (1958) for chlorine, and of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for the light atoms). Corrections for secondary extinction were made to the larger amplitudes by the method of Pinnock, Taylor & Lipson (1956). The three projections were then separately refined by difference syntheses, assuming individual isotropic temperature factors for the heavy atoms and an overall isotropic temperature factor for the light atoms. The final agreement indices were $R_{h0l}=0{\cdot}110$, $R_{hk0}=0{\cdot}079$, $R_{0kl}=0{\cdot}083$. The resulting coordinates were consistent, and no one of the difference maps showed any feature which suggested the structure to be other than correct and complete. The electron density projection on (010) is shown in Fig. 1, this being particularly definitive in that it is centrosymmetric, with all but 6 of 315 terms sign determined by the platinum atom.

Subsequently it became possible to complete the three-dimensional refinement, using the IBM 7070 structure-factor and differential-synthesis programs written by R. Shiono. Only the 1358 reflexions with $\sin\theta < 0{\cdot}8$ were utilized. Several refinement cycles were performed, with atomic coordinates and isotropic temperature factors for the heavy atoms only as the variable parameters. Individual isotropic light atom parameters were introduced in the final cycle only. The final R value was 0·087. Three-dimensional Fourier and difference Fourier syntheses were then calculated. The electron-density synthesis exactly reproduced the postulated structure, but the various spurious peaks which appeared in the previous three-dimensional syntheses were still present. These disappeared completely from the difference synthesis, which confirmed their assignment as series termination effects. Small, sharp peaks did, however, appear at $(0, \pm\frac{3}{8}, 0)$. These were never apparent in the electron density syntheses and were much smaller in volume than the atom peaks. Their nearest approaches to the molecule are in each case to atom C(18), being 2·61 and 2·15 Å respectively. It was thus not meaningful to assign either peak as an atom of the molecule, or as a further molecule of water of crystallisation. It is probable that they are accumulations of error resulting from the poor quality of some of the higher layer photographs, and they were ignored. Apart from them the residual density never excedeed 1·2 Å^{-3}, and seldom exceeded 0·5 e.Å^{-3}. One such region, which was within bonding distance of O(6) was tested by assuming it to be a carbon atom with a high temperature factor (6·0 Å^2). The overall R value increased to 0·093, and more significantly R for reflexions with $\sin\theta < 0{\cdot}4$, to which such an atom would make greatest contribution, increased from 0·090 to 0·105. A subsequent difference synthesis showed a hollow deeper than the height of the original peak.

The structure was then subjected to further tests in which various atoms [C(16), C(17), C(18), O(6), O(7) and O(8)], separately, or in small groups, were omitted from the structure factor calculations. In each case the omitted atom or atoms appeared in a subsequent difference synthesis as a dominant peak, and those atoms which are designated as oxygen gave rise to the largest such peaks even when not included in the structure factors.

Table 1. *Atomic coordinates and temperature factors*

Atom	x	y	z	B
Pt	0	0	0	2·7
Cl(1)	0·0042	−0·0009	0·1235	4·9
Cl(2)	0·1196	0·1651	0·0027	5·1
Cl(3)	0·1194	−0·1641	0·0031	5·1
O(1)	0·3305	−0·2835	0·3053	4·5
O(2)	0·2177	−0·4053	0·2462	5·5
O(3)	0·0997	−0·4148	0·3530	5·2
O(4)	0·2679	0·1727	0·3800	6·2
O(5)	0·2712	0·0234	0·2879	4·6
O(6)	0·5126	−0·0344	0·2341	5·6
N	0·3879	0·0523	0·1499	6·2
C(1)	0·2974	−0·0343	0·1170	6·6
C(2)	0·3109	−0·1529	0·1504	6·8
C(3)	0·3648	−0·1667	0·2004	5·8
C(4)	0·3911	−0·2947	0·2425	5·4
C(5)	0·2481	−0·3470	0·3022	4·6
C(6)	0·1925	−0·3521	0·3638	5·1
C(7)	0·2525	−0·4451	0·4178	6·7
C(8)	0·1813	−0·2045	0·3926	6·2
C(9)	0·1271	−0·2043	0·4679	6·0
C(10)	0·1213	−0·1193	0·3381	5·7
C(11)	0·1333	0·298	0·3523	5·2
C(12)	0·0588	0·1106	0·3785	4·9
C(13)	0·0671	0·2362	0·4086	6·0
C(14)	0·2337	0·0856	0·3442	4·7
C(15)	0·3729	0·0613	0·2746	5·2
C(16)	0·3761	0·2126	0·2440	6·1
C(17)	0·4120	−0·0211	0·2167	5·2
C(18)	0·4833	0·0475	0·1037	6·7
$H_2O(7)$	0·2201	−0·4713	0·1048	6·6
$H_2O(8)$	0·1094	0·2924	0·1692	6·3

Table 2. *Interatomic distances and bond angles*

Bond lengths

C(1)–C(2)	1·34 Å	C(11)–C(12)	1·42 Å
C(2)–C(3)	1·16	C(12)–C(13)	1·37
C(3)–C(4)	1·53	C(11)–C(14)	1·57
C(4)–O(1)	1·51	C(14)–O(4)	1·17
O(1)–C(5)	1·29	C(14)–O(5)	1·36
C(5)–O(2)	1·25	O(5)–C(15)	1·48
C(5)–C(6)	1·44	C(15)–C(16)	1·60
C(6)–O(3)	1·42	C(15)–C(17)	1·50
C(6)–C(7)	1·56	C(17)–O(6)	1·41
C(6)–C(8)	1·56	C(17)–C(3)	1·59
C(8)–C(9)	1·66	C(17)–N	1·47
C(8)–C(10)	1·52	N–C(18)	1·63
C(10)–C(11)	1·50	N–C(1)	1·59
Pt–Cl(1)	2·33	Pt–Cl(2)	2·31
	Pt–Cl(3)	2·30	

Table 2 (*cont.*)

Bond angles

N–C(1)–C(2)	102·6°	C(10)–C(11)–C(12)	122·7°
C(1)–C(2)–C(3)	122·7	C(10)–C(11)–C(14)	115·5
C(2)–C(3)–C(4)	129·1	C(12)–C(11)–C(14)	121·3
C(2)–C(3)–C(17)	105·5	C(11)–C(12)–C(13)	128·2
C(17)–C(3)–C(4)	125·2	C(11)–C(14)–O(5)	108·2
C(3)–C(4)–O(1)	103·0	C(11)–C(14)–O(4)	123·0
C(4)–O(1)–C(5)	127·9	O(4)–C(14)–O(5)	128·7
O(1)–C(5)–O(2)	119·4	C(14)–O(5)–C(15)	116·8
O(1)–C(5)–O(6)	120·1	O(5)–C(15)–C(16)	110·7

Bond angles

O(2)–C(5)–C(6)	120·5	O(5)–C(15)–C(17)	112·4
C(5)–C(6)–O(3)	114·9	C(16)–C(15)–C(17)	103·0
C(5)–C(6)–C(7)	104·7	C(15)–C(17)–C(3)	118·1
C(5)–C(6)–C(8)	109·1	C(15)–C(17)–N	106·9
C(7)–C(6)–O(3)	104·9	C(15)–C(17)–O(6)	106·4
C(7)–C(6)–C(8)	113·0	O(6)–C(17)–N	113·4
C(3)–C(6)–C(8)	110·1	O(6)–C(17)–C(3)	109·2
C(6)–C(8)–C(10)	110·6	N–C(17)–C(3)	103·1
C(6)–C(8)–C(9)	111·8	C(17)–N–C(18)	107·9
C(9)–C(8)–C(10)	108·7	C(17)–N–C(1)	100·3
C(8)–C(10)–C(11)	113·8	C(18)–N–C(1)	113·4
Cl(1)–Pt–Cl(2)	91·1	Cl(2)–Pt–Cl(3)	89·8
	Cl(1)–Pt–Cl(3)	90·7	

Table 3. *Observed and calculated structure factors*

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
0	0	4	58	78	0	10	0	39	39	−1	3	14	53	45	2	0	7	60	68
0	0	5	179	194	0	10	1	35	32	1	3	15	52	46	−2	0	7	105	125
0	0	6	167	184	0	10	2	31	29	−1	3	15	58	53	2	0	8	141	164
0	0	7	194	198	0	10	3	28	29	1	3	16	78	70	−2	0	8	94	111
0	0	8	271	208	0	10	4	27	29	−1	3	16	39	40	2	0	9	90	99
0	0	9	168	194	1	1	0	116	142	1	3	17	47	41	−2	0	9	179	190
0	0	10	117	136	1	1	1	97	136	−1	3	17	49	46	2	0	10	82	86
0	0	11	105	116	1	1	2	255	266	1	3	18	27	25	−2	0	10	71	63
0	0	12	81	86	−1	1	2	255	252	−1	3	18	37	35	2	0	11	59	66
0	0	13	106	98	1	1	3	218	209	1	5	0	125	136	−2	0	11	66	50
0	0	14	97	87	−1	1	3	177	194	1	5	1	93	104	2	0	12	41	36
0	0	15	86	70	1	1	4	70	85	−1	5	1	111	129	−2	0	12	109	104
0	0	16	80	80	−1	1	4	93	109	1	5	2	125	142	2	0	13	39	31
0	0	17	90	98	1	1	5	153	173	−1	5	2	98	109	−2	0	13	83	82
0	0	18	65	57	−1	1	5	74	83	1	5	3	104	118	2	0	14	66	60
0	0	19	48	44	1	1	6	147	173	−1	5	3	108	111	−2	0	14	61	59
0	2	0	196	236	−1	1	6	151	170	1	5	4	98	96	2	0	15	70	62
0	2	1	178	198	1	1	7	123	141	−1	5	4	68	68	−2	0	15	87	89
0	2	2	81	72	−1	1	7	176	194	1	5	5	68	54	2	0	16	69	64
0	2	3	114	133	1	1	8	118	127	−1	5	5	105	90	−2	0	16	69	67
0	2	4	35	38	−1	1	8	142	167	1	5	6	88	78	2	0	17	55	53
0	2	5	33	31	1	1	9	99	109	−1	5	6	120	112	−2	0	17	69	61
0	2	6	42	53	−1	1	9	137	148	1	5	7	116	136	2	0	18	41	35
0	2	7	115	83	1	1	10	116	131	−1	5	7	93	92	−2	0	18	91	71
0	2	8	128	147	−1	1	10	93	105	1	5	8	117	105	2	0	19	33	28
0	2	9	119	141	1	1	11	65	67	−1	5	8	126	114	−2	0	19	54	42
0	2	10	67	59	−1	1	11	104	107	1	7	0	94	103	2	2	0	165	185
0	2	11	52	59	1	1	12	60	62	1	7	1	89	93	2	2	1	155	147
0	2	12	34	28	−1	1	12	69	70	−1	7	1	96	114	−2	2	1	157	164
0	2	14	77	70	1	1	13	68	79	1	7	2	61	75	2	2	2	129	150
0	2	15	61	54	−1	1	13	34	45	−1	7	2	78	92	−2	2	2	69	76
0	2	16	43	42	1	1	14	64	70	1	7	3	72	82	2	2	3	132	150
0	2	17	41	56	1	−1	14	51	57	−1	7	3	78	66	−2	2	3	55	54
0	2	18	52	50	1	1	15	62	69	1	7	4	65	59	2	2	4	44	29
0	2	19	21	26	1	−1	15	93	104	−1	7	4	60	61	−2	2	4	130	136
0	4	0	151	156	1	1	16	64	67	1	7	5	63	64	2	2	5	106	114
0	4	1	109	118	1	−1	16	84	102	−1	7	5	69	65	−2	2	5	103	108
0	4	2	61	56	1	1	17	76	73	1	7	6	88	78	2	2	6	97	101
0	4	4	72	73	1	−1	17	54	57	−1	7	6	90	82	−2	2	6	140	148
0	4	5	17	18	1	1	18	42	44	1	7	7	68	75	2	2	7	81	100
0	4	6	34	33	1	−1	18	56	55	−1	7	7	84	84	−2	2	7	67	71
0	4	7	95	107	1	1	19	31	27	1	7	8	92	78	2	2	8	156	173
0	4	8	85	75	1	−1	19	44	46	−1	7	8	109	92	−2	2	8	95	97
0	4	9	76	82	1	3	0	63	68	1	9	0	51	59	2	2	9	97	100
0	4	10	80	84	1	3	1	62	58	1	9	1	43	44	−2	2	9	109	122
0	4	11	37	38	−1	3	1	95	124	−1	9	1	32	34	−2	2	10	91	98
0	4	12	26	30	1	3	2	67	84	1	9	2	38	41	2	2	11	70	64
0	4	13	46	40	−1	3	2	43	60	1	9	3	30	28	−2	2	11	30	36
0	4	14	39	35	1	3	3	75	94	−1	9	3	38	36	2	2	12	41	39
0	4	15	39	43	−1	3	3	58	59	1	9	4	18	21	−2	2	12	54	43
0	4	16	48	46	1	3	4	72	54	−1	9	4	23	21	2	2	13	73	75
0	4	17	51	53	−1	3	4	76	74	1	9	5	28	25	−2	2	13	80	73
0	4	18	26	37	1	3	5	57	54	−1	9	5	30	30	2	2	14	55	125
0	6	0	141	157	−1	3	5	54	39	1	9	6	28	31	−2	2	14	60	58
0	6	1	150	156	1	3	6	114	124	−1	9	6	28	32	2	2	15	57	67
0	6	2	117	124	−1	3	6	73	55	1	9	7	38	39	−2	2	15	48	51
0	6	3	97	97	1	3	7	64	74	−1	9	7	31	37	2	2	16	73	76
0	6	4	101	99	−1	3	7	75	96	1	9	8	35	44	−2	2	16	60	65
0	6	5	97	105	1	3	8	76	57	−1	9	8	28	37	2	2	17	36	38
0	6	6	120	111	−1	3	8	82	81	2	0	0	60	62	−2	2	17	64	64
0	6	7	108	116	1	3	9	64	67	−2	0	1	201	213	2	2	18	42	39
0	6	8	124	110	−1	3	9	47	45	−2	0	2	26	51	−2	2	18	50	47
0	8	0	49	49	1	3	10	50	51	2	0	3	97	110	2	4	0	129	159
0	8	1	57	58	−1	3	10	46	42	−2	0	3	172	171	2	4	1	149	159
0	8	2	53	56	1	3	11	76	58	2	0	4	101	114	−2	4	1	80	97
0	8	3	34	48	−1	3	11	55	43	−2	0	4	137	147	2	4	2	74	75
0	8	4	45	40	1	3	12	34	31	2	0	5	176	210	−2	4	2	90	109
0	8	5	42	38	−1	3	12	49	35	−2	0	5	71	80	2	4	3	34	43
0	8	6	48	48	1	3	13	49	44	2	0	6	45	40	−2	4	3	100	98
0	8	7	44	49	1	3	14	42	39	−2	0	6	168	182 •	2	2	10 •	72	61

Table 3 (*cont.*)

h	k	l	Fo	Fo	h	k	l	Fo	Fc	h	k	l	Fo	Fo	h	k	l	Fo	Fc
2	4	4	115	121	3	1	1	146	140	3	3	18	62	54	4	0	10	64	81
2	4	4	66	54	-3	1	1	222	204	-3	3	18	47	48	-4	0	10	84	83
2	4	5	98	103	3	1	2	53	43	3	5	0	89	84	4	0	13	30	32
-2	4	5	94	100	-3	1	2	118	121	3	5	1	125	130	4	0	14	21	21
2	4	6	77	92	3	1	3	30	33	-3	5	1	99	105	-4	0	14	32	29
-2	4	6	91	89	-3	1	3	56	57	3	5	2	71	88	4	0	15	26	23
2	4	7	75	81	3	1	4	52	50	-3	5	2	87	86	-4	0	15	34	31
-2	4	7	88	91	-3	1	4	65	79	3	5	3	50	58	4	0	16	58	49
2	4	8	93	101	3	1	5	37	31	-3	5	3	51	62	-4	0	16	67	57
-2	4	8	118	133	-3	1	5	76	78	3	5	4	58	56	4	0	17	43	34
2	4	9	97	114	3	1	6	71	80	-3	5	4	47	46	-4	0	17	60	54
-2	4	9	80	91	-3	1	6	93	100	3	5	5	57	61	4	0	18	30	27
2	4	10	70	64	3	1	7	111	148	-3	5	5	57	51	-4	0	18	49	42
-2	4	10	49	48	-3	1	7	119	124	3	5	6	71	71	4	2	0	285	281
2	4	11	46	46	3	1	8	102	119	-3	5	6	100	81	4	2	1	211	215
-2	4	11	51	46	-3	1	8	112	155	3	5	7	63	71	-4	2	1	179	173
2	4	12	54	58	3	1	9	58	67	-3	5	7	94	101	4	2	2	114	143
-2	4	12	59	60	-3	1	9	73	75	3	5	8	93	97	-4	2	2	112	122
2	4	13	55	47	3	1	10	52	54	-3	5	8	69	52	4	2	3	78	80
-2	4	13	64	58	-3	1	10	85	101	3	7	0	73	80	-4	2	3	70	82
2	4	14	59	57	3	1	11	57	56	3	7	1	50	47	4	2	4	126	133
-2	4	14	46	43	-3	1	11	55	71	-3	7	1	63	66	-4	2	4	114	151
2	4	15	54	53	3	1	12	23	30	3	7	2	52	57	4	2	5	78	81
-2	4	15	56	58	-3	1	12	30	25	-3	7	2	50	52	-4	2	5	109	95
2	4	16	50	56	-3	1	13	47	48	3	7	3	45	46	4	2	6	81	75
-2	4	16	59	61	3	1	14	47	46	-3	7	3	46	49	-4	2	6	95	90
2	4	17	48	53	-3	1	14	57	60	-3	7	4	46	41	4	2	7	138	152
-2	4	17	60	50	3	1	15	47	55	3	7	5	47	52	-4	2	7	131	142
2	6	0	80	86	-3	1	15	58	63	-3	7	5	30	25	4	2	8	107	129
2	6	1	112	122	3	1	16	47	52	3	7	6	35	36	-4	2	8	142	146
-2	6	1	84	96	-3	1	16	67	74	-3	7	6	66	66	4	2	9	96	110
2	6	2	50	71	3	1	17	40	38	3	7	7	39	44	-4	2	9	145	169
-2	6	2	83	87	-3	1	17	54	57	-3	7	7	63	67	4	2	10	97	112
2	6	3	57	56	3	1	18	42	43	3	7	8	70	63	-4	2	10	102	112
-2	6	3	62	62	-3	1	18	32	36	-3	7	8	55	44	4	2	11	52	64
2	6	4	75	73	3	3	0	169	188	3	9		52	61	-4	2	11	78	78
-2	6	4	99	98	3	3	1	165	172	3	9	1	68	69	4	2	12	55	61
2	6	5	54	59	-3	3	1	205	193	-3	9	1	63	67	-4	2	12	78	81
-2	6	5	76	76	3	3	2	167	170	3	9	2	64	66	4	2	13	61	66
2	6	6	82	80	-3	3	2	232	219	-3	9	2	65	59	-4	2	13	61	59
-2	6	6	64	57	3	3	3	104	108	3	9	3	50	46	4	2	14	46	47
2	6	7	68	67	-3	3	3	196	182	-3	9	3	54	54	-4	2	14	36	43
-2	6	7	74	82	3	3	4	145	159	3	9	4	55	51	4	2	15	42	55
2	6	8	88	69	-3	3	4	91	84	-3	9	4	53	50	-4	2	15	54	61
-2	6	8	112	96	3	3	5	93	105	3	9	5	48	52	4	2	16	56	61
2	8	0	77	73	-3	3	5	58	47	-3	9	5	45	53	-4	2	16	72	79
2	8	1	44	46	3	3	6	99	110	3	9	6	40	41	4	2	17	55	62
-2	8	1	73	69	-3	3	6	155	150	-3	9	6	52	52	-4	2	17	76	81
2	8	2	57	62	3	3	7	176	196	3	9	7	47	57	4	2	18	33	35
-2	8	2	59	58	-3	3	7	140	159	-3	9	7	48	47	-4	2	18	55	57
2	8	3	52	52	3	3	8	129	128	3	9	8	64	62	4	4	0	138	149
-2	8	3	43	50	-3	3	8	125	129	-3	9	8	66	56	4	4	1	147	151
2	8	4	39	33	3	3	9	108	115	4	0	0	37	47	-4	4	1	155	172
-2	8	4	46	39	-3	3	9	138	139	4	0	1	33	33	4	4	2	127	114
2	8	5	57	55	3	3	10	123	118	-4	0	1	100	97	-4	4	2	123	127
-2	8	5	54	52	-3	3	10	129	125	4	0	2	87	81	4	4	3	117	121
2	8	6	50	49	3	3	11	88	35	-4	0	2	49	38	-4	4	3	91	93
-2	8	6	44	46	-3	3	11	69	63	4	0	3	22	20	4	4	4	78	77
2	8	7	56	59	3	3	12	69	60	-4	0	3	62	50	-4	4	4	100	100
-2	8	7	52	48	-3	3	12	59	58	4	0	4	33	30	4	4	5	68	70
2	8	8	64	54	3	3	13	59	57	-4	0	4	40	26	-4	4	5	93	100
-2	8	8	73	61	-3	3	13	67	67	-4	0	5	34	69	4	4	6	114	123
2	10	0	45	49	3	3	14	65	59	4	0	6	30	14	-4	4	6	96	90
2	10	1	41	41	-3	3	14	69	64	-4	0	6	92	72	4	4	7	93	108
-2	10	1	52	49	3	3	15	72	74	4	0	7	45	48	-4	4	7	107	[illegible]
2	10	2	38	40	-3	3	15	84	82	-4	0	7	93	105	4	4	8	92	[illegible]
-2	10	2	44	45	3	3	16	64	62	4	0	8	44	43	-4	4	8	125	134
2	10	3	33	33	-3	3	16	75	72	-4	0	8	115	133	4	4	9	91	[illegible]
-2	10	3	47	41	3	3	17	67	64	4	0	9	60	77	-4	4	9	100	[illegible]
3	1	0	176	183	-3	3	17	66	60	-4	0	9	63	56	4	4	10	82	[illegible]

Table 3 (*cont.*)

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fo	h	k	l	Fo	Fc
-4	4	10	97	110	5	1	12	37	36	-5	7	2	59	60	-6	2	5	92	92
4	4	11	65	68	-5	1	12	36	35	5	7	3	27	26	6	2	6	82	83
-4	4	11	77	79	5	1	13	39	42	-5	7	3	40	38	-6	2	6	70	67
4	4	12	48	51	-5	1	13	21	[illegible]	5	7	4	61	62	6	2	7	63	72
-4	4	12	60	60	5	1	14	43	50	-5	7	4	47	44	-6	2	7	101	112
4	4	13	37	38	-5	1	14	59	64	5	7	5	28	31	6	2	8	93	100
-4	4	13	51	50	5	1	15	51	58	-5	7	5	51	51	6	2	8	125	136
4	4	14	55	58	-5	1	15	59	62	5	7	6	36	29	6	2	9	73	76
-4	4	14	62	64	5	1	16	39	40	-5	7	6	36	31	-6	2	9	110	119
4	4	15	61	59	-5	1	16	46	54	5	7	7	53	56	6	2	10	48	60
-4	4	15	67	70	5	1	17	36	35	-5	7	7	38	37	-6	1	10	76	69
4	4	16	56	55	-5	1	17	43	44	5	7	8	54	45	6	2	11	47	53
-4	4	16	45	56	5	1	18	27	30	-5	7	8	69	57	-6	2	11	70	67
4	4	17	36	42	-5	1	18	36	41	5	9	0	59	67	6	2	12	49	55
-4	4	17	57	65	5	3	0	155	168	5	9	1	55	55	-6	2	12	56	58
4	6	0	65	63	5	3	1	138	141	-5	9	1	88	73	6	2	13	31	37
4	6	1	45	42	-5	3	1	161	153	5	9	2	57	58	-6	2	13	50	58
-4	6	1	39	45	5	3	2	132	131	-5	9	2	32	57	6	2	14	28	29
4	6	2	47	51	-5	3	2	178	180	5	9	3	52	52	-6	2	14	41	53
-4	6	2	47	48	5	3	3	138	143	-5	9	3	51	53	6	2	15	36	45
4	6	3	42	49	-5	3	3	109	105	5	9	4	46	41	-6	2	15	55	62
-4	6	3	34	40	5	3	4	102	108	-5	9	4	50	47	6	2	16	42	43
4	6	4	24	21	-5	3	4	121	118	5	9	5	44	46	-6	2	16	75	76
-4	6	5	24	14	5	3	5	105	115	-5	9	5	55	51	6	2	17	37	42
4	6	6	47	44	-5	3	5	164	158	5	9	6	48	51	-6	2	17	54	60
-4	6	6	18	26	5	3	6	138	143	-5	9	6	46	52	6	4	0	104	114
4	6	7	42	52	-5	3	6	131	131	6	0	0	69	63	6	4	1	85	87
-4	6	7	55	58	5	3	7	88	95	6	0	1	100	104	-6	4	1	75	81
4	6	8	51	47	-5	3	7	150	154	-6	0	1	169	172	6	4	2	69	62
-4	6	8	71	60	5	3	8	129	126	6	0	2	73	82	-6	4	2	88	91
4	8	0	73	79	-5	3	8	157	155	-6	0	2	121	117	6	4	3	75	80
4	8	1	63	71	5	3	9	105	107	6	0	3	98	84	6	4	3	106	102
-4	8	1	69	76	-5	3	9	117	117	-6	0	3	16	3	6	4	4	49	54
4	8	2	57	57	5	3	10	71	52	6	0	4	99	92	-6	4	4	56	55
-4	8	2	45	54	-5	3	10	94	97	-6	0	4	55	50	6	4	5	59	50
4	8	3	46	48	5	3	11	57	56	-6	0	5	94	83	-6	4	5	55	55
-4	8	3	25	54	-5	3	11	94	95	6	0	6	42	56	6	4	6	72	73
4	8	4	67	58	5	3	12	55	57	-6	0	6	99	95	-6	4	6	82	83
-4	8	4	55	57	-5	3	12	73	72	6	0	7	115	138	6	4	7	69	71
4	8	5	48	49	5	3	13	63	61	-6	0	7	38	31	-6	4	7	70	75
-4	8	5	52	48	-5	3	13	76	73	6	0	8	82	86	6	4	8	76	77
4	8	6	55	57	5	3	14	61	60	-6	0	8	93	92	-6	4	8	100	96
-4	8	6	62	56	-5	3	14	71	77	6	0	9	82	80	6	4	9	58	69
4	8	7	55	66	5	3	15	58	59	-6	0	9	100	107	-6	4	9	93	92
-4	8	7	51	64	-5	3	15	86	88	6	0	10	61	56	6	4	10	55	38
4	8	8	58	53	5	3	16	54	51	-6	0	10	96	87	-6	4	10	79	84
-4	8	8	79	67	-5	3	16	85	81	6	0	11	49	48	6	4	11	57	46
5	1	0	65	68	5	3	17	45	41	-6	0	11	40	34	-6	4	11	47	49
5	1	1	111	110	-5	3	17	59	62	6	0	12	53	45	6	4	12	40	38
-5	1	1	78	78	5	5	0	75	78	-6	0	12	24	21	-6	4	12	37	38
5	1	2	92	105	5	5	1	66	70	6	0	13	45	42	-6	4	13	51	56
-5	1	2	81	85	-5	5	1	92	95	-6	0	13	56	49	6	4	14	24	33
5	1	3	50	49	5	5	2	54	48	6	0	14	40	35	-6	4	14	41	43
-5	1	3	70	74	-5	5	2	56	54	-6	0	14	40	39	6	4	15	37	35
5	1	4	27	34	5	5	3	49	55	6	0	15	64	56	-6	4	15	45	53
-5	1	4	64	55	-5	5	3	22	23	-6	0	15	46	44	6	6	0	76	78
5	1	5	79	98	5	5	4	61	42	6	0	16	55	49	6	6	1	71	71
-5	1	5	93	91	-5	5	4	58	60	-6	0	16	78	67	-6	6	1	58	54
5	1	6	90	100	5	5	5	54	52	6	0	17	44	32	6	6	2	49	59
-5	1	6	121	125	-5	5	5	76	65	-6	0	17	58	55	-6	6	2	68	71
5	1	7	79	83	5	5	6	73	70	6	2	0	106	123	6	6	3	42	43
-5	1	7	84	94	-5	5	6	48	45	6	2	1	133	133	-6	6	3	51	51
5	1	8	58	53	5	5	7	58	66	-6	1	1	148	154	6	6	4	39	35
-5	1	8	77	73	-5	5	7	76	73	6	2	2	78	78	-6	6	4	48	31
5	1	9	45	65	5	5	8	63	40	-6	2	2	150	153	6	6	5	61	62
-5	1	9	9	67	-5	5	8	86	79	6	2	3	58	53	-6	6	5	55	49
5	1	10	55	62	5	7	0	22	40	-6	2	3	77	76	6	6	6	57	56
-5	1	10	52	51	5	7	1	69	64	6	2	4	82	89	-6	6	6	66	58
5	1	11	36	35	-5	7	1	60	59	-6	2	4	70	65	6	6	7	45	44
-5	1	11	57	63	5	7	2	53	56	6	2	5	76	90	-6	6	7	57	56

Discussion

Atomic coordinates are in Table 1, bond lengths and angles in Table 2, and observed and calculated structure factors in Table 3. The mean standard deviations in atomic coordinates (Cruickshank, 1949, 1950) are 0·01 Å for chlorine and 0·05 Å for the light atoms.

The allocation of atoms as carbon, nitrogen and oxygen is discussed above. Even within the wide limits of error the bond C(2)–C(3), of measured length 1·16 Å, must be a double bond. Assuming on chemical grounds that bond C(11)–C(12) is also double, and that apart from those of the carbonyl groups all others are single, the formula of the molecule is $(C_{18}H_{28}NO_6)_2PtCl_6 . 2H_2O$, the structural formula of the cation being as (I). The above double bond assignments are supported by the observation that the atoms of each of the groups C(1), C(2), C(3), C(4), C(17) and C(10), C(11), C(12), C(13), C(14) are coplanar.

The structure of the necic acid, including the relative configurations of the two asymmetric carbon atoms C(5) and C(6), is identical with that established by X-ray methods for the related alkaloid jacobine (Fridrichsons, Mathieson & Sutor, 1963). The methyl group C(13) is *cis* to the carbonyl group C(14)–O(4), and the acid is thus defined as senecic acid.

The acid is esterified to the necine through the atoms C(4) and C(15). The base is atypical of *senecio* alkaloids in that its nucleus is a single five-membered ring rather than two fused rings. The free base would systematically be described 1-methyl-2-hydroxy-2-(1′-hydroxyethyl)-3-hydroxymethyl-3-pyrroline.

The chloroplatinate ion is regularly octohedral within the limits of error.

The hydroxyl oxygen atom O(6) makes a hydrogen bond approach of 2·73 Å to hydroxyl oxygen O(3′) of the molecule related by the *C* centring translation, as shown in Fig. 1. The same atom O(6) makes an approach of 2·54 Å to the water molecule O(8), the angles about O(6) being C(17)–O(6)–O(3′), 120·1°; C(17)–O(6)–O(8), 120·1°; O(8)–O(6)–O(3′), 118·8. The water molecule O(7) makes a contact of 2·76 Å with hydroxyl oxygen O(2′) [of the same molecule that contains O(3′)]. The two water molecules are separated by 3·09 Å, and are thus not linked by other than a very

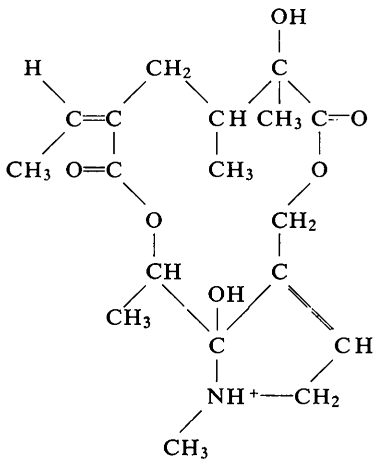
Table 3 (*cont.*)

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fo
6	6	8	72	74	7	3	10	48	47	-8	0	13	40	42	-8	6	7	75	73
-6	6	8	65	57	-7	3	10	76	76	8	0	14	55	47	8	6	8	66	61
6	8	0	54	62	7	3	11	22	25	-8	0	14	79	69	-8	6	8	84	73
6	8	1	61	62	-7	3	11	58	55	8	0	15	53	45	8	8	0	24	33
-6	8	1	61	59	-7	3	12	44	39	-8	0	15	84	71	8	8	1	36	40
6	8	2	62	54	-7	3	13	30	26	8	2	0	85	102	-8	8	1	44	46
-6	8	2	50	57	7	3	14	29	27	8	2	1	31	44	8	8	2	41	37
6	8	3	39	36	-7	3	14	44	38	-8	2	1	80	81	-8	8	2	39	42
-6	8	3	55	60	7	3	15	34	36	8	2	2	43	46	8	8	3	30	34
6	8	4	50	42	-7	3	15	44	45	-8	2	2	58	60	-8	8	3	32	35
-6	8	4	46	39	7	5	0	82	95	8	2	3	78	83	8	8	4	30	29
6	8	5	46	49	7	5	1	71	79	-8	2	3	51	51	-8	8	4	35	34
-6	8	5	50	46	-7	5	1	72	71	8	2	4	35	29	9	1	0	61	60
6	8	6	41	45	7	5	2	58	58	-8	2	4	31	26	9	1	1	82	77
-6	8	6	54	57	-7	5	2	87	94	8	2	5	43	39	-9	1	1	106	109
6	8	7	45	49	7	5	3	58	57	-8	2	5	48	41	9	1	2	110	118
-6	8	7	48	55	-7	5	3	77	76	8	2	6	54	55	-9	1	2	97	100
6	8	8	61	49	7	5	4	56	49	-8	2	6	49	41	9	1	3	71	70
-6	8	8	61	57	-7	5	4	42	33	8	2	7	52	51	-9	1	3	96	88
7	1	0	144	161	7	5	5	54	50	-8	2	7	95	100	9	1	4	45	56
7	1	1	129	137	-7	5	5	36	36	8	2	8	55	44	-9	1	4	78	92
-7	1	1	106	112	7	5	6	69	67	-8	2	8	92	91	9	1	5	78	85
7	1	2	86	85	-7	5	6	78	71	8	2	9	51	56	-9	1	5	70	64
-7	1	2	112	115	7	5	7	71	68	-8	2	9	51	56	9	1	6	80	82
7	1	3	65	62	-7	5	7	73	73	8	2	10	29	40	-9	1	6	99	99
-7	1	3	134	132	7	5	8	63	58	-8	2	10	59	65	9	1	7	59	64
7	1	4	60	67	-7	5	8	65	79	8	2	11	22	23	-9	1	7	82	90
-7	1	4	64	59	7	7	0	78	82	-8	2	11	44	45	9	1	8	63	64
7	1	5	68	66	7	7	1	64	69	8	2	12	31	36	-9	1	8	71	71
-7	1	5	73	62	-7	7	1	70	71	8	2	13	33	31	9	1	9	56	59
7	1	6	96	93	7	7	2	47	53	8	2	14	24	34	-9	1	9	88	109
-7	1	6	90	88	-7	7	2	63	65	-8	2	14	46	52	9	1	10	54	56
7	1	7	95	102	7	7	3	67	63	8	2	15	26	26	-9	1	10	48	59
-7	1	7	91	94	-7	7	3	57	59	-8	2	15	48	51	9	1	11	35	42
7	1	8	87	97	7	7	4	52	36	8	4	0	70	70	-9	1	11	50	55
-7	1	8	115	122	-7	7	4	59	55	8	4	1	42	45	9	1	12	26	29
7	1	9	82	93	7	7	5	49	48	-8	4	1	80	85	-9	1	12	58	55
-7	1	9	87	102	-7	7	5	61	57	8	4	2	48	48	9	1	13	78	31
7	1	10	59	63	7	7	6	69	65	-8	4	2	31	42	-9	1	13	36	41
-7	1	10	81	91	-7	7	6	43	40	8	4	3	43	41	9	1	14	31	40
7	1	11	49	54	7	7	7	46	50	8	4	4	33	36	9	1	14	33	47
-7	1	11	67	72	-7	7	7	75	71	-8	4	4	40	36	9	3	0	51	48
7	1	12	33	37	7	7	8	54	53	8	4	5	39	35	9	3	1	52	45
-7	1	12	45	50	-7	7	8	83	71	-8	4	5	53	46	-9	3	1	25	31
7	1	13	33	33	8	0	0	185	201	8	4	6	48	40	9	3	2	42	39
-7	1	13	49	52	8	0	1	134	139	-8	4	6	54	46	-9	3	2	50	44
7	1	14	45	48	-8	0	1	138	132	8	4	7	44	47	9	3	3	25	30
-7	1	14	54	56	8	0	2	79	83	-8	4	7	51	51	-9	3	3	50	41
7	1	15	72	50	-8	0	2	91	93	8	4	8	65	70	9	3	4	21	3
-7	1	15	47	50	8	0	3	114	106	-8	4	8	69	67	-9	3	4	25	29
7	1	16	40	47	-8	0	3	98	102	8	4	9	27	29	9	3	5	46	49
-7	1	16	42	58	8	0	4	123	131	-8	4	9	60	63	-9	3	5	37	33
7	3	0	84	85	-8	0	4	114	108	-8	4	10	36	38	9	3	6	55	55
7	3	1	94	100	8	0	5	83	70	-8	4	11	44	40	9	3	7	35	34
-7	3	1	87	72	-8	0	5	114	106	-8	4	12	32	29	-9	3	7	44	42
7	3	2	64	61	8	0	6	101	98	-8	4	13	37	32	-9	3	8	70	64
-7	3	2	58	49	-8	0	6	132	121	8	6	0	79	91	-9	3	9	40	34
-7	3	3	64	67	8	0	7	110	107	8	6	1	64	62	9	3	10	38	35
7	3	4	33	24	-8	0	7	110	103	-8	6	1	99	99	-9	3	10	37	37
-7	3	4	56	49	8	0	8	88	83	8	6	2	69	82	-9	3	11	35	28
7	3	5	38	38	-8	0	8	137	138	8	6	2	71	67	-9	3	12	27	20
-7	3	5	43	36	8	0	9	94	91	8	6	3	73	72	-9	3	13	27	24
7	3	6	52	50	-8	0	9	134	134	-8	6	3	74	69	-9	3	14	19	22
-7	3	6	61	55	8	0	10	65	58	8	6	4	56	59	9	3	15	34	34
7	3	7	61	58	-8	0	10	94	82	-8	6	4	84	77	9	5	0	62	65
-7	3	7	73	66	8	0	11	67	56	8	6	5	70	64	9	5	1	76	74
7	3	8	64	66	-8	0	11	106	99	-8	6	5	72	67	-9	5	1	73	71
-7	3	8	57	53	8	0	12	76	70	8	6	6	61	57	9	5	2	64	64
7	3	9	53	53	-8	0	12	64	61	-8	6	6	79	71	-9	5	2	73	78
-7	3	9	82	78	8	0	13	56	52	8	6	7	66	69	9	5	3	67	51

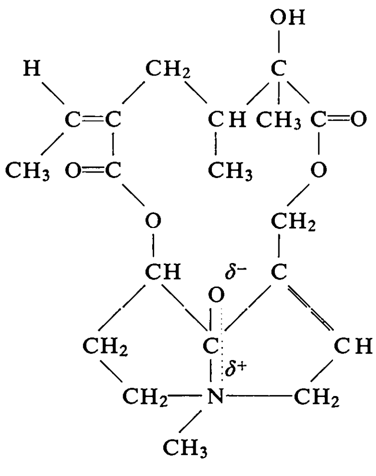
Table 3 (*cont.*)

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
-9	5	3	69	60	-10	2	6	79	72	11	1	5	31	31	12	0	9	29	26
9	5	4	72	59	10	2	7	63	65	11	1	6	42	43	-12	0	9	34	37
-9	5	4	69	61	-10	2	7	[illegible]	[illegible]	-11	1	6	25	[illegible]	12	2	0	51	53
9	5	5	58	53	10	2	8	63	64	-11	1	7	46	52	12	2	1	54	56
-9	5	5	66	66	-10	2	8	42	49	-11	1	7	84	73	-12	2	1	65	61
9	5	6	61	53	10	2	9	37	44	-11	1	8	65	64	12	2	2	44	56
-9	5	6	55	50	-10	2	9	70	79	-11	1	9	37	41	-12	2	2	45	51
9	5	7	56	48	10	2	10	29	33	11	1	10	29	36	12	2	3	43	44
-9	5	7	68	64	-10	2	10	56	67	-11	1	10	61	65	12	2	4	45	45
9	5	8	64	61	10	2	11	22	30	11	1	11	22	24	-12	2	4	64	57
-9	5	8	92	83	-10	2	11	19	[illegible]	-11	1	11	41	45	12	2	5	36	41
9	7	0	61	65	10	2	12	15	21	11	3	0	60	63	-12	2	5	68	68
9	7	1	56	59	-10	2	12	[illegible]	25	11	3	1	63	65	12	2	6	56	46
-9	7	1	45	50	10	4	0	61	67	-11	3	1	69	70	-12	2	6	40	42
9	7	2	51	45	10	4	1	57	64	11	3	2	65	58	12	2	7	39	37
-9	7	2	45	45	-10	4	1	70	66	-11	3	2	68	71	-12	2	7	45	48
9	7	3	43	36	10	4	2	34	42	11	3	3	48	40	12	2	8	35	40
-9	7	3	54	55	-10	4	2	52	55	-11	3	3	71	64	-12	2	8	64	64
9	7	4	39	39	10	4	3	33	32	11	3	4	56	52	12	2	9	39	42
-9	7	4	40	38	-10	4	3	43	46	-11	3	4	41	40	-12	2	9	53	59
9	7	5	44	42	10	4	4	52	44	11	3	5	44	41	12	4	0	52	59
9	7	6	37	33	-10	4	4	43	44	-11	3	5	35	31	12	4	1	48	49
-9	7	6	57	57	10	4	5	45	46	11	3	6	55	48	-12	4	1	47	56
-10	0	0	100	123	-10	4	5	40	40	-11	3	6	67	65	12	4	2	37	42
10	0	1	91	93	10	4	6	36	37	11	3	7	63	66	-12	4	2	40	51
-10	0	1	109	108	-10	4	6	61	51	-11	3	7	68	62	12	4	3	46	48
10	0	2	57	47	10	4	7	45	45	11	3	8	45	44	-12	4	3	39	44
-10	0	2	79	76	-10	4	7	65	56	-11	3	8	71	64	12	4	4	36	41
10	0	3	51	43	10	4	8	50	52	11	3	9	32	34	-12	4	4	48	48
-10	0	3	50	42	-10	4	8	46	53	-11	3	9	61	61	12	4	5	47	41
10	0	4	50	42	10	4	9	39	45	11	3	10	31	38	-12	4	5	52	53
-10	0	4	74	66	-10	4	9	48	56	-11	3	10	44	47	12	4	6	45	42
10	0	5	68	60	10	4	10	53	40	11	5	0	52	60	-12	4	6	43	43
-10	0	5	72	61	-10	4	10	46	52	11	5	1	39	40	13	1	0	30	37
10	0	6	64	62	-10	4	11	37	44	-11	5	2	45	48	13	1	1	46	44
-10	0	6	76	64	-10	4	12	23	29	11	5	[illegible]	45	43	-13	1	1	24	35
10	0	7	37	34	10	6	0	52	56	-11	5	2	39	40	13	1	2	26	24
-10	0	7	98	95	10	6	1	51	56	11	5	3	50	44	-13	1	2	46	53
10	0	8	97	92	-10	6	1	52	54	-11	5	3	51	54	13	1	3	28	24
-10	0	8	82	77	10	6	2	37	44	11	5	4	22	23	-13	1	3	29	32
10	0	9	56	53	-10	6	2	66	62	-11	5	4	35	35	13	1	4	23	21
-10	0	9	96	90	10	6	3	38	34	11	5	5	31	33	-13	1	5	35	32
-10	0	10	74	68	-10	6	3	51	52	11	5	6	41	40	13	1	6	33	36
10	0	11	43	42	10	6	4	40	39	-11	5	6	54	43	-13	1	6	29	36
-10	0	11	49	47	-10	6	4	43	40	11	5	7	40	36	13	3	0	49	57
10	0	12	52	36	10	6	5	43	40	-11	5	7	49	47	13	3	1	42	44
-10	0	12	62	53	-10	6	5	46	51	12	0	0	34	31	-13	3	1	58	60
10	0	13	29	24	10	6	6	41	39	-12	0	1	40	33	13	3	2	50	49
-10	0	13	63	52	-10	6	6	54	43	12	0	2	36	36	-13	3	2	62	61
10	2	0	71	73	10	6	7	43	42	-12	0	2	27	24	13	3	3	48	44
10	2	1	53	60	-10	6	7	52	52	12	0	3	33	33	-13	3	3	50	49
-10	2	1	72	76	11	1	0	49	55	-12	0	3	19	30	13	3	4	35	37
10	2	2	45	49	11	1	1	53	39	12	0	4	27	20	-13	3	4	46	46
-10	2	2	43	50	-11	1	1	61	63	-12	0	4	28	22	13	3	5	41	40
10	2	3	36	34	11	1	2	38	37	12	0	5	22	25	-13	3	5	46	49
-10	2	3	50	50	-11	1	2	53	57	-12	0	5	34	23	14	0	0	38	30
10	2	4	54	48	11	1	3	25	[illegible]	-12	0	6	34	35	14	0	1	45	35
-10	2	4	35	30	-11	1	3	51	51	12	0	7	23	27	-14	0	1	38	35
10	2	5	39	34	11	1	4	41	44	-12	0	7	48	44	-14	0	2	47	44
-10	2	5	37	38	-11	1	4	60	56										

weak hydrogen bond. Both water molecules make close approaches to atoms of the chloroplatinate ion, *viz.* O(7) - - - Cl(2), 3·39 Å; O(8) - - - Cl(1), 3·32 Å O(8) - - - Cl(2), 3·40 Å. Other close contacts involving the chlorine atoms are Cl(3) - - - C(1), 3·38 Å, and Cl(1) - - - C(17), 3·49 Å.



(I)



(II)

Senkirkine has now been shown (Briggs, Cambie, Candy, O'Donovan, Russell & Seelye, 1965) to be identical with renardine (Danilova, Koretskaya & Utkin 1961), and is considered to have the same necine base as has been established by X-ray analysis (Wunderlich, 1962) to exist in retusamine. The structural formula is then as (II). This differs from (I) in that atoms N and C(16) are connected by a further methylene group. The nuclear magnetic resonance spectrum of senkirkine is considered to be consistent with this, and quite inconsistent with the structure deduced from this work. All the electron density syntheses were again scrutinized in the appropriate region, but no suggestion of an omitted atom could be found. It is thus deduced that the compound studied in this work is not a salt of senkirkine. Numerous attempts were then made to prepare the compound again so that its relationship to senkirkine might be established. The crystals which resulted whenever the original preparation was repeated were reproducible but were quite distinct from those which have been described herein, and no one of the many variations attempted was any more successful. This failure has thwarted further investigation, but there are two obvious possibilities. The molecule may have decomposed to lose a methylene group under the particular conditions of the original preparation, although it is difficult to postulate a mechanism for such a change. It should be noted, however, that it has not yet proved possible to regenerate senkirkine from any sample of its chloroplatinate. Alternatively the compound may be one of the minor alkaloids, several of which are known to exist in *Senecio kirkii*. It is hoped that further work on these alkaloids will elucidate this question.

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