tated by hydrazine hydrochloride were distilled separately in hydrogen and the atomic weight determinations gave the following:

		Det. No.	Wt. of Te. Gms.	Wt. of $TeBr_4$. Gms.	% of Te.	At. wt. of Te.
A	Fraction Nos. 1, 2, 3 and 4....	1	0.300558	1.054251	28.509	127.481
A	Fraction Nos. 1, 2, 3 and 4....	2	0.199807	0.700947	28.505	127.456
B	Fraction Nos. 1, 2, 3 and 4....	1	0.22032	0.773048	28.500	127.425
B	Fraction Nos. 1, 2, 3 and 4....	2	0.158161	0.554717	28.512	127.500
Fraction No. 19.....		1	0.436907	1.532360	28.512	127.500
Fraction No. 19.....		2	0.29811	1.045485	28.514	127.512
Average.....					28.509	127.479

These determinations show that there is no separation of the tellurium after 19 fractional precipitations by hydrazine hydrochloride and that there is no difference between the tellurium which crystallized from the nitric acid solution in the octahedral crystals as the dioxide and that separating in the orthorhombic crystals as the basic nitrate.

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CORRECTION.

The papers from this laboratory which appeared in the June JOURNAL require the following corrections:

P. 712, equation 75, for 2RT read $\frac{2n_a RT}{F}$, and p. 739, lines 33 and 37, for mm. read cm.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WYOMING.]

ANALYSES OF SOME WYOMING LARKSPURS. I.

BY F. W. HEYL, F. E. HEPNER AND S. K. LOY.

Received May 17, 1913.

The poisonous character of some of the various larkspurs which are widely and abundantly distributed in the states of the Northwest has been the subject of several experimental studies. Chestnut and Wilcox[1] studied the influence of *Delphinium glaucum* and of *Delphinium bicolor* upon animals which were fed with these plants or with extracts prepared from them. These workers also had the opportunity for observing, to some extent, the economic importance of these particular species in Montana. During the season of 1900, one hundred cases of cattle poisoning produced by *Delphinium glaucum* were brought to their attention and of these fifty-six proved fatal. Because of the habitat of this plant on the mountain ranges, cattle alone are poisoned by it. The figures given are

[1] Div. Bot., U. S. Dept. Agr., *Bull.* 26, 65 (1901).

stated to be approximately one-fourth of the total loss caused by this plant in Montana.

A study of the larkspurs of Colorado by Dr. Geo. H. Glover[1] and C. Dwight Marsh indicates that this genus is considered second only to loco from the standpoint of the economic loss produced in that state through poisonous plants. These workers consider *Delphinium Nelsonii*, *D. elongatum* (*glaucum*), *D. geyeri* and *D. barbeyi* as the most poisonous to stock, and of decreasing toxicity in the order named. One other study[2] of the poisonous properties of *D. glaucum* has been carried out by Dr. B. Kennedy of the Nevada Experiment Station.

In Wyoming the three important larkspurs are *Delphinium geyeri*, *D. glaucum* and *D. Nelsonii*. The only chemical work that has been carried out upon any of these is confined to the report[3] of an alkaloidal assay upon the roots of *D. Nelsonii*. This showed the presence of 0.72% of crude alkaloid. In the same work, the isolation of an alkaloid from the roots of *D. scopulorum* is described. It is a crystallin substance, melting at 184°–185° and has the formula $C_{23}H_{33}NO_7$. It is now placed upon the market by Merck, but the commercial product as described in Merck's "Index" is an amorphous white powder. It is used as a substitute for curare. In another communication[4] it is reported that the chemical examination of the roots of the various species of *Delphinium* proved the alkaloidal material to be similar.

These larkspurs are to be distinguished from those of European and of Asiatic origin, upon which considerable chemical work has been carried out.

In the present paper we report the proximate analyses of the different parts of the several species which are important in this state. Unless there is a marked difference in the physiological activities of the alkaloids in these species, it would seem from the results of our assays that *D. geyeri* is the most dangerous. In order to gain some idea as to the toxicity of the crude alkaloidal mixture obtained from the leaves of *D. geyeri* an intraperitoneal injection of 0.0564 gram of the alkaloid as sulfate was made upon a guinea pig weighing 675 grams. Death followed in nine minutes. In another experiment an intraperitoneal injection of 0.02 gram as sulfate killed a guinea pig weighing 623 grams in thirty-five minutes.[5]

However, the prevailing opinion as to the toxicity of these larkspurs

[1] *Bull. Co. Agr. Expt. Station*, 113, 24.

[2] *Bull. Nev. Agr. Expt. Sta.*, 55, 53, and others.

[3] Geo. Heyl, *Süddeutsche Apotheker Zeitung*, 43, 29 (1903).

[4] *Südd. Apotheker Zeitung*, 43, 28 (1903).

[5] The study of the physiological action of these alkaloidal preparations is being conducted by Dr. R. H. Prien and will be reported in a Bulletin from the Experiment Station.

does not ascribe to *D. geyeri* the position which our results would seem to indicate. Pammel,[1] for example, states that *D. elongatum* (*glaucum*) and *D. Nelsonii* are the only ones that contain a sufficient quantity of deleterious substance to produce poisoning. The leaves of the three species have been subjected to a complete proximate analysis. Since the leaves of *D. geyeri* contain a comparatively high alkaloid content, and furthermore since it is the most abundant species in Wyoming, a complete chemical investigation of the constituents will be carried out in this laboratory by Dr. Loy.

Experimental Part.

The tall larkspur (*D. glaucum*) was collected while in full bloom during the first week in August. The collection was made upon the Snowy Range near Centennial in the U. S. forest reservation. The leaves and stems were prepared as a single sample. The flowers and roots were separated and these were prepared in the usual manner.

The sample of *D. Nelsonii* was collected about the middle of June at Medicine Bow. Some of the plants were in full bloom and some were mature. The various parts were separated, dried in the air, and prepared for analysis in the usual manner.

Delphinium geyeri was collected in large quantities (120 kilograms) between May 15 and June 10, 1912, just east of Laramie. The plants did not flower during this period because of the exceedingly dry spring. We were, therefore, unable to carry out any analytical work beyond that described on the roots and leaves.

The samples were analyzed according to the usual[2] methods. The alkaloidal assays in the following table were made according to the method[3] given in the United States Pharmacopoeia for the assay of the belladonna leaves.

The Isolation of d-Mannitol.—The leaves of *Delphinium Nelsonii* were now assayed by a second method. A portion weighing 50 grams was extracted with one liter of 95 per cent. alcohol for several days. The mixture was occasionally brought to the boiling point. The tincture was removed by filtration on a Büchner funnel and the residue washed several times with alcohol and pressed dry. The filtrate was concentrated under reduced pressure to a small volume and allowed to stand over night, whereupon a poorly crystallin deposit weighing 1.37 grams separated.

The partially exhausted drug was boiled with alcohol exactly as before and upon concentrating this extract 0.95 grams of beautiful, colorless needles separated. The melting point was 158°–162°. Upon further recrystallization from alcohol the melting point remained constant at

[1] "Manual of Poisoning Plants," 467 (1911).

[2] U. S. Dept. Agr., Bur. of Chem., *Bull.* 107 (Revised).

[3] U. S. Dispensatory, 19th Ed., p. 228.

	D. nelsonii.					*D. glaucum.*			*D. geyeri.*	
	Flower.	Pod.	Seed.	Leaf.	Root.	Flower.	Leaf.	Root.	Leaf and stem.	Root.
Ligroin ext. 93°[2]	1.10	1.68	20.86	1.11	0.23	1.52	2.05	0.84	0.86	0.30
Ether ext. total	1.93	3.70	23.28[2]	1.87	0.41	3.70	3.08	0.95	2.25	0.79
Ether ext. volatil	0.05	0.12	0.46	0.02	0.02	0.20	0.15	0.04	0.06	0.05
Alcohol ext. 100°	42.04	29.19	...	34.89	31.83	35.17	28.06	26.96	32.46	16.48
Moisture	6.90	6.89	5.96	7.20	8.11	4.87	5.54	5.37	8.94	5.75
Starch (diastase)	none	none	none	none	20.08	none	none	2.54	none	7.20
Pentosans	11.31	14.58	9.62	13.04	7.32	12.74	12.42	17.63	11.70	11.84
Crude fiber	12.91	15.92	7.48	21.92	5.18	14.72	22.31	33.86	16.77	18.03
Protein	11.65	16.23	23.05	7.52	5.27	15.61	13.46	8.96	9.31	9.98
Ash	10.90	11.15	6.21	10.34	11.15	10.14	13.58	5.30	17.47	19.49
Crude alkaloid	0.79	0.60	1.27	0.34	0.48	0.77	0.62	1.79	1.15	0.93
Resin	...	...	...	2.00	...	...	2.28	...	2.19	...
Sucrose	...	...	...	3.83	...	...	1.15	...	1.69	...
Reducing sugar[1]	...	...	...	5.74	...	...	0.87	...	1.06	...
Dextrin	1.10	1.17	...	0.72	6.15	1.44	0.53	1.09	0.49	1.09

[1] Calculated as glucose.

[2] Iodine No. = 51.6.

165°. Analysis showed that the two crops consisted of *d*-mannitol. The following analyses were conducted upon samples obtained from *D. Nelsonii*, *D. geyeri* and *D. glaucum*, respectively:

Calculated for $C_6H_{14}O_6$: C, 39.6; H, 7.7.
Found: C, 39.77, 39.36, 39.5; H, 7.9, 7.8, 7.9.

The yield obtained is equivalent to 4.62% of the plant.

The alcoholic mother liquors were joined and made up to a volume of 250 cc. and the dissolved solids and carbohydrates were determined upon an aliquot portion. The remainder of this solution equivalent to 43 grams of the plant was used for an alkaloidal assay. The solution was concentrated to the consistency of a fluid extract and diluted with a mixture of 10 cc. of *N* sulfuric acid and 200 cc. water. The resin which precipitated weighed 0.8627 gram equivalent to 2.00%. The acid solution was extracted several times with the ether and then, after rendering it strongly ammoniacal, the alkaloid was extracted with ether. From the ether the alkaloid was removed by repeated extraction with 0.1 *N* sulfuric acid, from which it was again extracted after neutralization with ammonia, by repeated extraction with ether and then with chloroform, until at length complete extraction was indicated by the failure of the aqueous solution to respond to a test with Mayer's reagent. The extracts, upon evaporation, left a residue weighing 0.0828 gram.

The original ammoniacal liquid gave a positive test for alkaloid and a second series of extractions was carried out as before, using chloroform instead of ether. The residue here obtained weighed 0.0221 gram. When the residues were titrated they required, respectively, 1.14 cc. and 0.31 cc. 0.1 *N* sulfuric acid.

These crude alkaloidal products contained a small amount of resin. A quantity of normal sulfuric acid was added to each of the solutions which had been titrated as described above, and after filtering and uniting the filtrates, the alkaloid was precipitated with Mayer's reagent, of which about 3.3 cc. were required. The mercury salt was filtered off, washed with water, suspended in dilute sulfuric acid and decomposed with hydrogen sulfide. The mercuric sulfide was removed by filtration, the filtrate was warmed to expel the excess of hydrogen sulfide, and the alkaloid was recovered by another series of extractions with ether and with chloroform. The weight was 0.0733 gram equivalent to 0.17%.

The above-described method was employed in the assay of the leaves of *D. geyeri*. Thus two crops of *d*-mannitol were obtained. The first melted at 164° and weighed 0.67 gram. The second melted at 156–158° and weighed 0.87 gram. The yield is therefore equivalent to 3.08%. The resin precipitated weighed 0.9434 gram equivalent to 2.19%. Ether extracted 0.3444 gram and chloroform 0.0789 gram of crude alkaloid. These neutralized 3.24 cc. and 1.18 cc. of 0.1 *N* acid, respectively.

Precipitated by Mayer's reagent, of which about 16.9 cc. were required, a white flocculent mercury salt was obtained which yielded 0.2255 gram of alkaloid equivalent to 0.52 per cent.

The leaf of *D. glaucum* when assayed by this method yielded but one crop of *d*-mannitol that weighed 0.18 gram and melted at about 160°. Recrystallization from 95% of alcohol raised the melting point to 165°. The yield is therefore 0.36%. The determination of crude alkaloid in 43 grams of the plant showed that ether extracted 0.1608 gram that required 1.87 cc. 0.1 *N* sulfuric acid, after which chloroform extracted 0.0388 gram requiring 0.51 cc. 0.1 *N* sulfuric acid. These were purified in the usual manner and there was obtained 0.1358 gram, equivalent to 0.32%. The resin precipitated weighed 0.9802 gram or 2.28%.

An analysis of the ash of the leaves of *D. geyeri* by Mr. Fred V. Skinner gave the following results:

CO_2	22.40	22.38
Sand	1.13	1.13
Carbon	0.33	0.33
SiO_2 (soluble)	11.88	11.72
$Fe_2O_3 + Al_2O_3$	5.36	5.28
CaO	24.49	24.34
MgO	0.05	0.05
K_2O	22.42	22.39
Na_2O	1.88	1.93
P_2O_5	1.26	1.44
SO_3	3.26	3.38
Cl	0.42	0.42
H_2O	3.36	3.36
Summation	98.24	98.15

LARAMIE, WYOMING.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

ETHYL CYANOTARTRONATE AND ITS REACTIONS WITH AMINES.

BY RICHARD SYDNEY CURTISS AND LLOYD F. NICKELL.

Received April 26, 1913.

For some time the senior author and his co-workers have been interested in the reactions of the oxomalonic esters with substances having dissociable hydrogen, such as alcohols, amines, and halogen acids.[1] In continuation of this work we have tried the action of prussic acid on ethyl oxomalonate, and have studied the action of the cyanhydrin thus formed with different types of amines.

Ethyl oxomalonate, $O = C : (COOC_2H_5)_2$, is a greenish yellow oil which reacts vigorously with water, hence the reaction between it and

[1] Curtiss and Spencer, THIS JOURNAL, 31, 1053; Curtiss, Hill and Lewis, *Ibid.*, 33, 400; Curtiss and Strachan, *Ibid.*, 33, 396.