THE SEASONAL VARIATION OF ACIDITY, TOXICITY, AND ALKALOIDAL CONTENT OF THREE SPECIES OF LARKSPUR.

BY O. A. BEATH.

GENERAL DESCRIPTION.

The three species of larkspur selected in this investigation represent distinctive altitudes and habitats. The plains type (*Delphinium geyeri*), commonly called low larkspur, grows on the plains of Wyoming and Colorado at altitudes ranging from five to seven thousand feet. It usually appears during May, and under normal conditions of growth, may be found in full bloom the latter part of June. After the flowering stage the plant dries up and rapidly disappears from the range. This species is a dangerous one from the time it appears until the flowers are well developed.

The next species in order of elevation is represented by *Delphinium glaucescens*. This plant grows in the shaded areas of canyons and mountain sides at an altitude of about eight thousand feet. As a general rule this species appears in the early part of June and is in full bloom by the middle of July. On account of its habitat the plant remains fairly green until the seeds are well developed. The losses from this plant are insignificant.

Delphinium subalpinium (*D. barbeyi*), commonly called the "tall larkspur," grows at elevations ranging from nine to thirteen thousand feet. It grows largely in the open, although one may find occasional patches partially shaded. On account of the climatic conditions encountered at higher altitudes, this plant has a variable growing season. *D. subalpinium* is one of the most poisonous of the larkspurs.

ACIDITY.

The expressed juice of the larkspurs is strongly acidic, and if appreciably diluted the concentration increases. Wicke[1] reports the free acid of *D. consolida* to be aconitic acid. His conclusion was based upon the fact that the silver salt had the same chemical composition as silver aconate, therefore, aconitic acid. The native larkspurs yield an acid having the chemical composition of $C_6H_6O_6$, but having physical and chemical properties quite different from those exhibited by the normal acid. It appears to be one of the two possible isomers. The acid obtained from the native larkspurs melts at 166–7° C., is non-toxic and optically inactive. It is very soluble in ether, alcohol and water. The silver salt detonates when heated slightly. The ethyl ester boils under a pressure of 25 mm. at 171–2° C.

In addition to the free acid necessary to form the water-soluble salts (alkaloidal) the plant produces a considerable excess. The acid also enters into chemical combination with a crystalline alkaloid to produce an amorphous complex, the latter being much more potent than any of the crystalline derivatives.

Figure 1 illustrates in a general way the seasonal distribution of the uncombined acid. It is clear that in the early periods of development the relative quantity of acid is quite uniform for the three species. There is no apparent correlation between the seasonal variation of acid and crude alkaloid.

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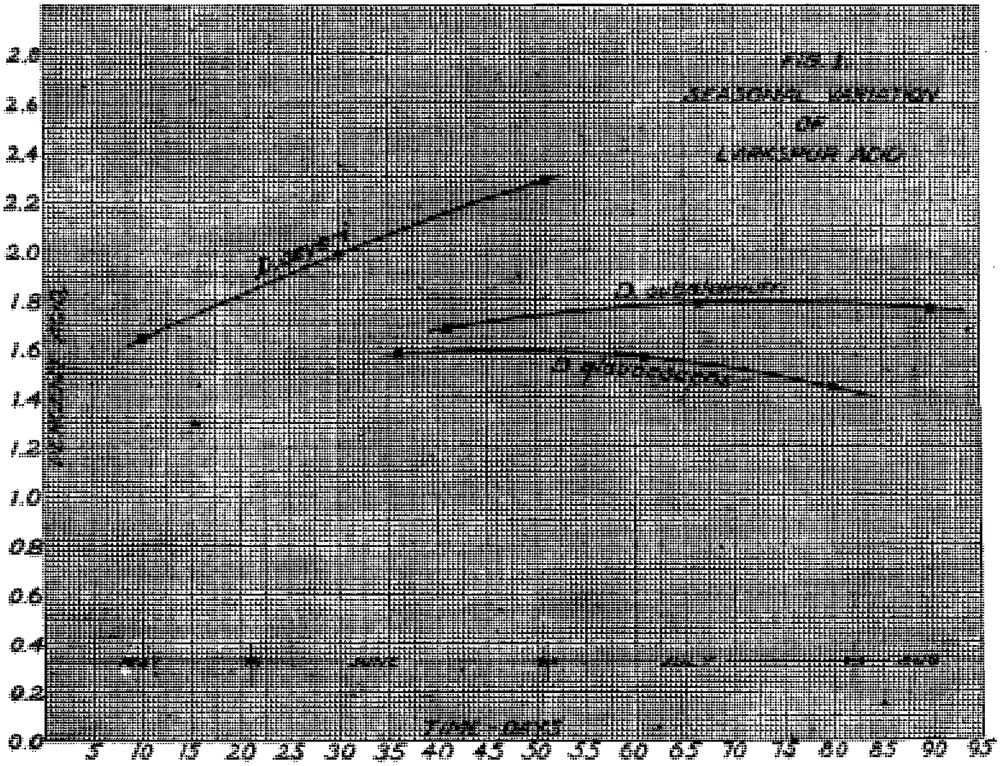
[1] *Annalen der Chemie*, Vol. 90, pp. 98–9.

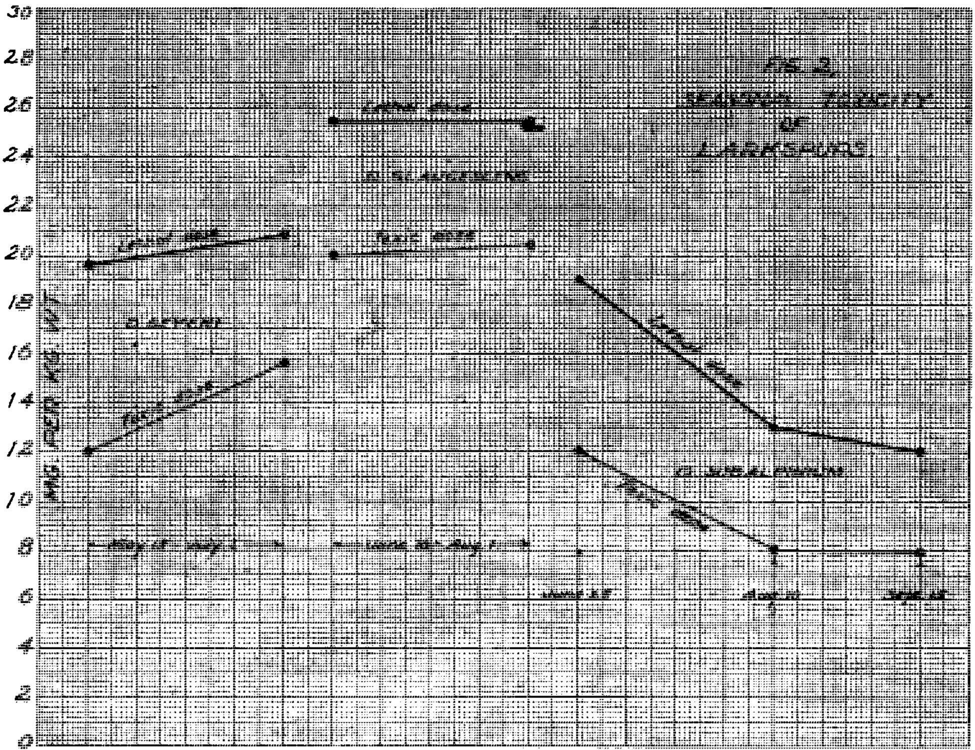


The relation of acid and toxicity will be discussed in another part of this paper.

TOXICITY.

The contributions relative to the seasonal variation of larkspur toxicity have not been consistent. The statement has been made, and seems to be borne out by range observers, that the larkspurs, as a rule, are more poisonous in the early stages of growth. Other contributing factors are involved while the plants are immature and must be carefully considered before final conclusions are drawn.

The experiments were undertaken to determine the period of maximum and minimum potency of the crude larkspur poisons at distinct stages of growth. The plants (whole) were carefully selected, dried, and reduced to a uniform powder. After percolating with alcohol the oils, fats, and resins were extracted with petroleum ether. The crude alkaloidal residues were taken up with seventy percent alcohol and made up to definite dilutions. The extracts were introduced intravenously into full-grown rabbits. The tests were made in duplicates and the average results tabulated. Figure II illustrates the relative amounts necessary to kill and to produce symptoms. *D. glaucescens* is shown to be much less poisonous than the other two species, although exhibiting no apparent change with the advance in growth. The tall larkspur differs from the other two types in that, as the flowering stage approaches, the lethal dose becomes comparatively small. The crude alkaloid of the seeds has practically the same value as that found in the whole plant (flowering stage).

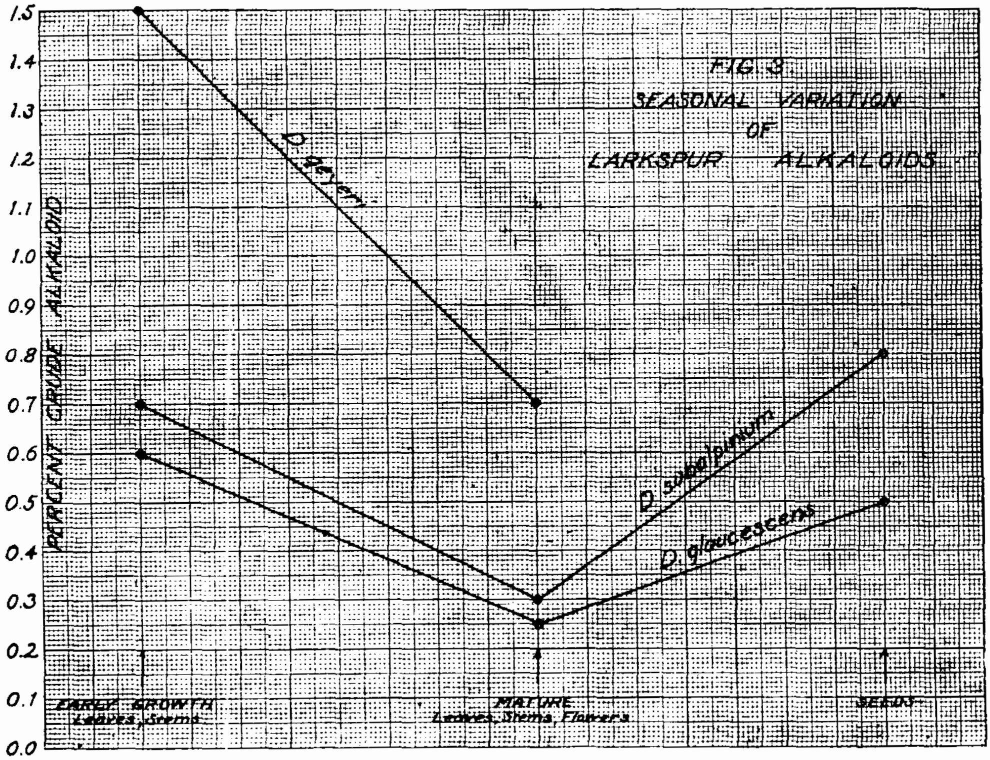


If the statement is correct that the larkspurs are more dangerous during the early periods of growth, clearly the cause is not due to greater toxicity.

D. geyeri and *D. subalpinium* are species representing the extreme conditions of growth, and yet the physical properties of the poisons obtained from them exhibit striking resemblances. *D. glaucescens*, the intermediate type, yields alkaloidal products markedly distinct from those of the other two species. The principal alkaloid is crystalline, optically active, has a structure much more complex than any other larkspur alkaloids and is present (crystalline form) in the plant at all stages of growth. Its physiological action closely resembles the low larkspur.

D. geyeri yields amorphous alkaloidal products only. In the early stages of growth, *D. subalpinium* yields one crystalline alkaloid, but it soon enters into combination with the plant acid to produce an amorphous product. The latter is very stable and requires saponification with alcoholic potash to resolve it into its constituents, acid and crystalline alkaloid. The toxicity of the amorphous complex is much greater than that of the simple base obtained from it. The low larkspur has the same general type of an amorphous alkaloid as found in the tall species. The crystalline alkaloid obtained by saponification is a new compound and differs from the other two bases in its physical and chemical properties. The pure alkaloid is very much less toxic than the amorphous complex from which it is derived.

The acid being non-toxic, it is interesting to observe that its combination with a slightly toxic base produces the intensely poisonous complex encountered in the two species. The alkaloids from *D. glaucescens* occur in the plant as salts. The corresponding amorphous complex is not formed in this plant.



SEASONAL VARIATION OF ALKALOIDS.

The determination of crude alkaloids in the larkspurs is attended with no difficulty if proper care is taken. It is necessary to use a mild alkali in breaking up the alkaloidal salts, otherwise decomposition follows and hence loss. The plant material was carefully selected, air dried, and reduced to a uniform powder. The moisture was determined on an aliquot portion, so that the percent of alkaloid has been computed on a bone-dry basis.

Figure 3 illustrates graphically the seasonal fluctuation. The three types follow the same general course, *D. geyeri* having the highest percent of any of the larkspurs. The seeds of this species were not obtainable. The pods of *D. subalpinium* and *D. glaucescens* contain far less alkaloid than the leaves and stems for the same period. As a rule the lowest alkaloidal content is reached when the plants are in full bloom. From this point on to the seeding stage, the percentage in the leaves and stems decreases somewhat while that in the seeds rapidly increase. An alkaloidal assay made on *D. subalpinium* at the time of seeding gave 0.25 percent of alkaloid in the leaves and stems, 0.20 percent in the pods, and 0.80 percent in the seeds.

The data indicate very clearly that the larkspurs are dangerous plants when immature, largely because of the quantity of alkaloid rather than its increased toxicity.

A Station bulletin is now being prepared giving the details obtained through a comprehensive chemical study of the larkspurs.

UNIVERSITY OF WYOMING AGRICULTURAL COLLEGE AND
EXPERIMENT STATION, LARAMIE, WYO.