TABLE X

PRODUCTS OF TREATMENT OF LIGNIN WITH NITRIC ACID

Substance		Phenol lignin	Methylin
Residue, g.	Total	9.5	6.5
	Water insol.	2.0	1.5
	Water, ether insol.	1.2	0.3
Silver salts		9.5	6.5
Raw picric acid		0.6	0.2

the silver chloride was concentrated to a very small volume, extracted with ether and the ether solution brought to dryness. The partly crystallized residue was dissolved in 20 cc. of concd. hydriodic acid and the solution kept in a sealed tube for six hours at 170–180°. On cooling the solution became turbid. The liquid was neutralized with sodium bicarbonate and then extracted with ether. The ether contained benzene, as established by applying the routine procedure.

Acknowledgment.—Acknowledgment is made to Dr. S. A. Waksman, of the Department of Soil Microbiology, New Jersey Agricultural Experiment Station, New Brunswick, New Jersey, who made possible the execution of this work.

Summary

1. A convenient method for preparing phenol lignin has been devised.

2. Phenol lignin and methoxy glycol lignin are closely related substances and represent mixtures which may be separated into several fractions, following the procedure developed.

3. These fractions have been characterized by chemical and physical determinations. As shown by potentiometric titrations, they are still mixtures consisting of several compounds.

4. A method for splitting off the phenol introduced into the phenol lignin has been developed.

5. On fusing with alkali, phenol lignin as well as methoxy glycol lignin give rise to protocatechuic acid and *p*-oxybenzoic acid; procedures of approximate quantitative determination have been devised for both of these acids.

6. On oxidizing with nitric acid, both phenol lignin and methoxy glycol lignin give rise to picric acid and benzene carboxylic acids; the latter were qualitatively established by decomposition, yielding benzene.

7. A formula has been given representing an ideal substance to which all chemical experiences collected in the investigation of spruce lignin may be traced and from which possibilities of further experimental work may be derived.

STATE COLLEGE, PENNSYLVANIA

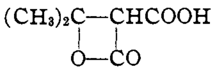
RECEIVED JANUARY 14, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Carbon Syntheses with Malonic Acid and Related Compounds. II. Aromatic Aldehydes

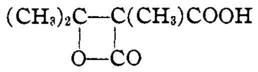
BY ARTHUR MICHAEL AND NATHAN WEINER

A large literature[1] exists on the use of malonic acid for the synthesis of α,β-unsaturated acids by condensation with aldehydes. Acetone does not show an analogous reaction; however, Meldrum[2] observed that the addition of a small amount of sulfuric acid to the mixture brought about an aldolization, involving the carbonyl group of the ketone, followed by an intramolecular esterification of the formed β-hydroxy acid to β,β-dimethyl-β-propiolactonic acid, (I). Ott[3] found the yield of lactonic acid considerably increased, if the sulfuric acid is first added to a suspension of malonic acid in acetic anhydride, the formed acetic acid and excess of anhydride removed by distillation *in vacuo* and the residual mixed malonic–acetic anhydride allowed to react with acetone. In this manner, Ott prepared α,β,β-trimethyl-β-propiolactonic acid, (II), from acetone and methylmalonic acid. By the Meldrum method, Khandiah[4] condensed malonic acid with di-isopropyl ketone, cyclopentanone and cyclohexanone and obtained the corresponding β-propiolactonic acids. Recently, Michael and Ross[1] showed that aliphatic aldehydes may be substituted for acetone in the Meldrum–Ott β-lactone synthesis. The present paper deals with the use of several aromatic aldehydes, *viz.*, benzoic, salicylic, acetylsalicylic and cinnamic aldehydes. These aldehydes cannot be used successfully in the Meldrum method, since



$$\begin{array}{l}(CH_3)_2C\text{—}CHCOOH\\ \;\;\;\;\;\;\;\;\;|\;\;\;\;\;\;\;|\\ \;\;\;\;\;\;\;\;\;O\text{—}CO\end{array}$$

(I)



$$\begin{array}{l}(CH_3)_2C\text{—}C(CH_3)COOH\\ \;\;\;\;\;\;\;\;\;|\;\;\;\;\;\;\;|\\ \;\;\;\;\;\;\;\;\;O\text{—}CO\end{array}$$

(II)

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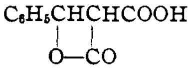
(1) See Michael and Ross, THIS JOURNAL, **55**, 3684 (1933).

(2) Meldrum, *J. Chem. Soc.*, **93**, 605 (1908); for explanation, see Michael and Ross, ref. 1, p. 3692.

(3) Ott, *Ann.*, **401**, 151 (1913).

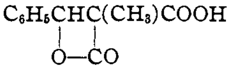
(4) Khandiah, *J. Chem. Soc.*, 1215 (1932).

under the reaction conditions, they react first with the anhydride to form benzal acetate or other inert compounds of the acetal type. By the Ott procedure, this complication is avoided and with malonic and methylmalonic acids, benzaldehyde gave 81 and 75% yields of β-phenyl-β-propiolactone-α-carboxylic acid, (III) and α-methyl-β-phenyl-β-propiolactone-α-carboxylic acid, (IV),



$$\begin{array}{l} C_6H_5CHCHCOOH \\ \;\;|\quad| \\ \;\;O{-}CO \end{array}$$

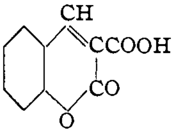
(III)



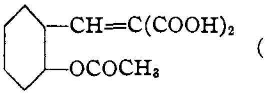
$$\begin{array}{l} C_6H_5CHC(CH_3)COOH \\ \;\;\;\;\;|\quad| \\ \;\;\;\;\;O{-}CO \end{array}$$

(IV)

respectively. With salicylic aldehyde a further complication arose, probably connected with the action of the phenolic hydroxyl upon the mixed acid anhydride formed in the Ott method. Although about 50% of unchanged malonic acid was recovered, a small yield of α-carboxycoumarin (V) was obtained. With acetylsalicylic aldehyde, a better yield of this acid was realized, along with a small quantity of *o*-acetoxybenzalmalonic acid, (VI). With these aldehydes it was not possible to prepare a β-lactonic acid. The formation of the coumarin derivative (V) is favored by the greater spatial proximity of the carboxyl to the *o*-hydroxy, or *o*-acetoxy, than to the β-hydroxy groups, which are thus enabled to participate more readily in the following intramolecular esterification. This results in an extremely stable hexacyclic derivative, in preference to the less easily formed and less stable 4-ring of a β-lactone derivative, and the formation of (V) and (VI) therefore proceeds with the maximum degradation of energy.

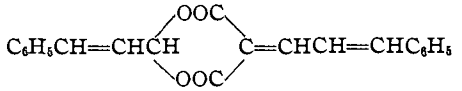


(V)



(VI)

Cinnamic aldehyde, although reacting with the malonic–acetic anhydride more vigorously than the other aromatic aldehydes, yielded a 30–35% yield of cinnamalmalonic acid, and much tarry by-product. In the preparation by the Meldrum method, some cinnamalmalonic acid and a neutral compound, $C_{21}H_{16}O_4$, were obtained. This compound must have been formed from two moles of cinnamic aldehyde and one of malonic acid, by the elimination of two moles of water. On treatment with alkali and subsequent acidification, it yielded cinnamalmalonic acid. With phenylhydrazine it gave almost the theoretical yield of cinnamic aldehyde phenylhydrazone. The compound, therefore, is the cinnamylidene ester of cinnamalmalonic acid, (VII). This structure was proved

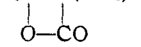


$$C_6H_5CH{=}CHCH\begin{array}{c} \diagup OOC \diagdown \\ \\ \diagdown OOC \diagup \end{array}C{=}CHCH{=}CHC_6H_5$$

(VII)

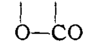
by the direct synthesis from cinnamalmalonic acid and cinnamic aldehyde, which was undoubtedly its mode of formation in the original system. The reaction shows that the outcome of the action of aldehydes upon malonic acid depends not only upon the presence of a mineral acid, but also upon the relative reactivity of the aldehyde.

The above β-propiolactonic acids, (III) and (IV), are the first definitely proved β-lactonic acid derivatives with only one substituent in the β-position. Ott[3] found that β,β-dimethyl-β-propiolactonic acid (I) decomposed thermally into acetone and ketene, and α,β,β-trimethyl-β-propiolactonic acid (II), under similar conditions, into acetone and high boiling products. This course of decomposition seemed anomalous to Salkowski,[5] since he had found that non-carboxylated β-lactones with one, two or no alkyls in the α-position, and either one or none in the β-position, are decomposed by heat into the corresponding alkenes and carbon dioxide. He believed that an essential difference should not exist between the properties of the simple β-propiolactones and the β-propiolactonic acid type of compound, and therefore ascribed the "ketone" decomposition of acids (I) and (II) to the presence of two alkyl groups at the β-carbon atoms. He did not take into account the negative, loosening influence of the additional α-carboxyl, and was unable to prepare a β-disubstituted propiolactone to test this opinion experimentally, The assumption seemed to find a support, when Michael and Ross[1] found that a reaction product, apparently α,β-dimethyl-β-propiolactone-α-carboxylic acid (VIII), decomposed thermally to α,β-dimethyl-β-propiolactone (IX) by



$$\begin{array}{l} CH_3CHC(CH_3)COOH \\ \;\;\;\;|\quad| \\ \;\;\;\;O{-}CO \end{array}$$

(VIII)



$$\begin{array}{l} CH_3CHCHCH_3 \\ \;\;\;\;|\quad| \\ \;\;\;\;O{-}CO \end{array}$$

(IX)

loss of carbon dioxide from the carboxyl group. However, in this case the lactonic acid was not isolated in a pure condition, nor was its structure definitely established. It seemed desirable to substantiate this mode of decomposition with an analogously constituted β-propiolactonic acid of known structure. We found that β-phenyl-β-propiolactone-α-carboxylic acid (III) did not give β-phenylpropiolactone on pyrolysis, but benzalde-

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(5) Salkowski, *J. prakt. Chem.*, **106**, 259 (1923).

hyde and acetic acid. Likewise the homologous α-methyl-β-phenyl-β-propiolactone-α-carboxylic acid (IV) yielded benzaldehyde and propionic acid. These results correspond, with regard to the formation of benzaldehyde, to the course of decomposition described by Ott and not with Salkowski's assumption. It seemed possible, however, that replacement of the β-methyl group of the propiolactonic acid (VIII) by phenyl so changed the affinity relationships that the "ketone" mode of decomposition is favored. We endeavored, therefore, to prepare acid (VIII) according to the directions of Michael and Ross.[1] They found that the reaction between paraldehyde and methylmalonic acid gave some α-methyl-β-hydroxy-α-carboxybutyric acid, and a viscous sirup as main product. The first compound on melting underwent fission at the α,β-carbons with formation of acetaldehyde and methylmalonic acid. The second product decomposed, on heating, largely to carbon dioxide and α,β-dimethyl-β-propiolactone (IX). We repeated the reaction according to the described Meldrum conditions, and also by the Ott method, but in each case the sirup gave only ethylidene acetate and propionic acid on distillation. Although the good yield of tiglic acid from the sirup, by heat, indicated the presence of the assumed acid (VIII), the assumed structure lacks direct experimental support, and the structure of the main product cannot be considered as definitely established.

However, there remains the fact that Michael and Ross must have isolated impure α,β-dimethyl-β-propiolactone (IX).[6] An explanation, perhaps, may be found in the observation of Hurd and Thomas[7] that benzaldehyde reacts with ketene to form, among other products, β-phenyl-β-propiolactone. If, as was assumed, the β-lactonic acid (VIII) was formed in the action of paraldehyde on methylmalonic acid, and, on heating, it decomposed to acetaldehyde and methyl ketene, there would have been present the components necessary for the synthesis of α,β-dimethyl-β-propiolactone (IX).

It has been observed[1] (p. 3690) that the relative stabilities of β-lactone rings toward heat and toward alkali run parallel to each other. β-Phenyl-β-propiolactone-α-carboxylic acid (III) and α-methyl-β-phenyl-β-propiolactone-α-carboxylic acid (IV) were treated with excess of 10% alkali and found to yield benzaldehyde and the malonic and methylmalonic salts, respectively. These lactones are therefore cleaved by alkali, through the corresponding β-hydroxy salts at the α,β-carbon linkage, just as by heat. Khandiah stated[4] that the similarly constituted lactones he prepared used up two equivalents of alkali upon treatment with an excess at 100° and yielded the salts of the corresponding substituted β-hydroxymalonic acids. In view of the reversibility of aldol polymerization in the presence of alkali, it seemed possible that Khandiah did not obtain the salts of the hydroxy acids, but malonate and the parent ketones. We investigated the action of alkali on one of Khandiah's compounds, *viz.*, β,β-pentamethylene-β-propiolactone-α-carboxylic acid and obtained a quantitative yield of cyclohexanone and malonate. Khandiah was probably likewise in error with regard to the other β-lactonic compounds, since he did not isolate any of the reaction products, but based his conclusions on results obtained by acid titration.

There appeared to be an exception to the generalization that the β-hydroxy salts are cleaved by alkali with rupture at the same carbon linkage as the corresponding free β-propiolactonic acids are on pyrolysis. Michael and Ross[1] reported that the sodium salt of α,β,β-trimethyl-β-propiolactonic acid (II) remained unattacked during evaporation of an aqueous alkaline solution. We reëxamined this reaction and found that unchanged lactonic acid can be recovered, at least to the extent of 95%, after treatment with an excess of 10% potash at 100° for ten to fifteen minutes. However, when the solution was kept under the same condition of alkalinity and temperature for several hours, cleavage of the salt into acetone and methyl malonate occurred. Therefore, all the β-propiolactonic acids are split by heat and the alkali β-lactonates by alkali, with fission at the α,β-carbons. A divergence from this rule can now be ascribed to constitutive properties, which affect only the relative facility of cleavage, not its definite course. After neutralization of the acidic groups, the course of alkali retrogression takes place by addition of water to the lactone group, to

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(6) Since Michael and Ross did obtain an excellent yield of a product, which, after saponification, gave almost the theoretical yield of tiglic acid upon heating, there can be no doubt of the accuracy of their results. Some of the malonic acid syntheses are exceedingly sensitive to slight experimental changes. For example, in the first experiment on the action of paraformaldehyde on malonic acid, we isolated β-acetoxypropionic acid from the reaction product in 25% yield, but in only one of five repetitions of the experiment could a much smaller yield be obtained.

(7) Hurd and Thomas, THIS JOURNAL, **55**, 275 (1933).

form the β-hydroxy salt. In that class of compounds the chemical hindrance to fission at the saturated α,β-carbons is slight, *e. g.*, even monobasic acids of the type $CH_3CHOHC(R)_2COOH$ undergo hydrolytic decomposition to aldehyde and dialkylacetic acids, upon heating with dilute sulfuric acid and $CH_3CHOHC(CH_3, C_3H_7)COOH$ undergoes retrogression to aldehyde and methylpropylacetic acid upon distillation. The concurrence of the negative carboxyl and hydroxyl groups at the α- and β-carbons, respectively, evidently greatly reduces their affinity for each other, which directs the course of decomposition, if the facile elimination of water is structurally prevented.

Experimental

General Procedure in the Ott Method.—The mixed anhydrides were prepared by suspending a weighed quantity of the acid in three times its weight of 95% acetic anhydride, adding 0.05–0.1 cc. of concentrated sulfuric acid and allowing the mixture to stand overnight. Addition of the sulfuric acid caused a decided fall in temperature and immediate solution of most of the acid. The formed acetic acid and excess of anhydride were then removed by heating, below 40°, in a water-bath at 2 mm. The carbonyl compound was then added to the sirupy residue and the mixture cooled with tap water.

β-Phenyl-β-propiolactone-α-carboxylic Acid (III).—Twenty-five g. of malonic acid and 26 g. of benzaldehyde were treated in the above manner. The mixture solidified soon after the addition of the aldehyde. The solid was broken up under ether and filtered; weight, 32.4 g. The mother liquor yielded, on standing, an additional 5 g. of the same compound. The substance was purified by recrystallization from an acetone–benzene mixture, from which it separated in glittering rhomboidal plates. It is soluble in acetone and chloroform and only sparingly in ether, petroleum ether and benzene. It turns brown at 135°, begins to decompose at 145°, and melts at 148°, with vigorous decomposition; yield, 81%.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.5; H, 4.17; neutral equiv. (monobasic), 192. Found: C, 62.84, 62.55; H, 4.66, 4.41; neutral equiv., 190.6, 191.2.

α-Methyl-β-phenyl-β-propiolactone-α-carboxylic Acid, (IV).—Twenty-two grams of methylmalonic acid and 20 g. of benzaldehyde were treated as described above. The reaction mixture, which solidified on cooling, was broken up under ether and filtered; weight, 26.8 g. of solid. An additional 2 g. was obtained from the mother liquor. It was recrystallized from an acetone–benzene mixture, m. p. 176–178°, with decomposition. It crystallizes in rhomboidal plates and is soluble in hot acetone and chloroform, only sparingly in ether, petroleum ether and benzene; yield, 75%.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.08; H, 4.85; neutral equiv. (monobasic), 206. Found: C, 63.93, 63.48; H, 4.96, 4.98; neutral equiv., 206, 206.

α-Carboxycoumarin (V) and *o*-Acetoxybenzalmalonic Acid (IV).—When salicylic aldehyde was added to the mixed malonic–acetic anhydride, heat was evolved and the mixture became extremely viscous. Some solid separated, which was filtered and identified as malonic acid (50% of the original acid). On standing, there was obtained a considerable quantity of "anhydrosalicylaldehyde" and a small amount of a substance, which was identified as α-carboxycoumarin by its melting point, 192°, and mixed melting point with an authentic sample. When an equivalent quantity of *o*-acetoxybenzaldehyde was added to the malonic–acetic anhydride, the mixture also became extremely viscous, and, on standing, a quantity of α-carboxycoumarin crystallized out (about a 25% yield). On dilution of the mother liquor with ether some flocculent material was precipitated (2 g. from 24 g. of malonic acid). This was recrystallized from benzene containing about 10% of acetone, and was obtained in groups of flocculent needles, which melted at 163° with decomposition.

Anal. Calcd. for $C_{12}H_{10}O_6$: C, 57.61; H, 4.0; neutral equiv. (dibasic), 125. Found: C, 57.66; H, 4.21; neutral equiv., 123.

Cinnamalmalonic Acid.—The mixed anhydride, prepared from 15.6 g. of malonic acid, was treated with 20 g. of freshly distilled cinnamic aldehyde. The mixture warmed decidedly at the first addition, and, as it could not be cooled sufficiently with tap water, the remainder of the aldehyde was added slowly in about an hour, with the mixture cooled in a freezing mixture. Notwithstanding, it turned black, with some decomposition, since a gas was evolved. When the mixture no longer warmed up on removal from the ice, the thick, tarry product was dissolved in a small volume of acetone, and the solution was poured into saturated sodium bicarbonate solution. The insoluble material was filtered and dried, but no crystalline product could be separated. The bicarbonate solution was acidified and gave 11.2 g. of a dry acid. It was identified as cinnamalmalonic acid by its melting point, 208°, and other properties; yield, 35%.

Cinnamylidene Cinnamalmalonate (VII).—11.4 g. of malonic acid was suspended in 25 cc. of acetic anhydride, and 14 g. of cinnamic aldehyde, followed by three drops of concentrated sulfuric acid, was added. The mixture warmed spontaneously, and was cooled in running tap water. The solution turned deep purple, which slowly changed to green. On standing overnight, 6.2 g. of a lemon-yellow compound was deposited, which after recrystallization from benzene–petroleum ether, melted at 157° with slow decomposition. The compound crystallizes in needles, is sparingly soluble in ether and petroleum ether, fairly in cold, and very soluble in hot benzene.

Anal. Calcd. for $C_{21}H_{16}O_4$: C, 75.92; H, 4.82. Found: C, 75.59, 75.85; H, 4.76, 4.91.

Reaction with Sodium Hydroxide.—The above compound is insoluble in sodium carbonate and in cold sodium hydroxide; 0.1 g. was suspended in 10 cc. of 10% sodium hydroxide solution and heated to boiling. The solid dissolved to an orange-yellow solution, which was cooled, acidified and extracted with ether. The ether extract deposited cinnamalmalonic acid, on concentration, which was identified by mixed m. p. with an authentic sample.

Reaction with Phenylhydrazine.—One gram of the yellow compound was suspended in 20 cc. of a mixture of equal parts of ether and benzene and 2 g. of phenylhydrazine in 10 cc. of ether added. After three hours, 1.6 g. of a voluminous solid, melting at 130–140°, was filtered off. Concentration of the mother liquor yielded 0.85 g. of a yellow compound, which after recrystallization from alcohol was identified as cinnamic aldehyde phenylhydrazone, by a mixed m. p. with an authentic sample. The lower melting compound was white, and after one recrystallization from alcohol melted at 138–140°. It was not investigated further and was probably the phenylhydrazide of cinnamalmalonic acid.

Synthesis of Cinnamylidene Cinnamalmalonate.—Two grams of cinnamalmalonic acid was suspended in a mixture of 4 g. each of acetic acid and acetic anhydride and 1.2 g. of cinnamic aldehyde, and two drops of sulfuric acid was added. The mixture warmed and became purple, slowly turning to green. On standing overnight a solid crystallized out. The solution was diluted with ether and filtered. The solid weighed 1.7 g. and an additional 0.5 g. was obtained from the mother liquor. After recrystallization from benzene–petroleum ether, the compound proved to be identical with the previously obtained cinnamylidene cinnamalmalonate.

Thermal Decomposition of β-Lactonic Acids.—Ten grams of β-phenyl-β-propiolactone-α-carboxylic acid (III) was heated at 160° in a distilling flask until the evolution of gas ceased. The volatile decomposition product was collected, the residue heated under reduced pressure and the two distillates united. The 3.3 g. of liquid distillate was fractionated at atmospheric pressure. It gave 0.5 g. of acetic acid, identified as acetanilide, and an oil, which was shown to be benzaldehyde by conversion to the semicarbazone.

Ten grams of α-methyl-β-phenyl-β-propiolactone-α-carboxylic acid (IV) was likewise decomposed at 190° and yielded 4 g. of liquid. Fractionation gave 0.6 g. of propionic acid, identified as propiotoluidide, and 3.3 g. of benzaldehyde.

Alkaline Cleavage of the Propiolactonic Acids.—The above two β-propiolactone-α-carboxylic acids, (III) and (IV), α,β,β-trimethylpropiolactonic acid (II) and β,β-pentamethylene-β-propiolactone-α-carboxylic acid were treated with alkali as follows: $^1/_{40}$ of one mole was dissolved in a solution of 4.2 g. of potassium hydroxide in 40 cc. of water and heated on the steam-bath for an hour. One equivalent of semicarbazide hydrochloride was then added and the solutions heated for four hours. With the two first acids, the precipitation of benzaldehyde semicarbazone was immediate, but with the two following the respective semicarbazones separated only upon cooling. The yield of benzaldehyde semicarbazone in each case was about 60%, that of cyclohexanone semicarbazone was quantitative, while acetone semicarbazone was obtained in only 25% yield. Acidification of the aqueous filtrates, repeated extraction of the solutions with ether and concentration of the extracts yielded practically the theoretical yields of malonic and methylmalonic acids.

Summary

1. It has been shown that benzaldehyde may replace acetone in the Ott synthesis of β-lactonic acids from malonic acid. Salicylic aldehyde does not thus lead to the formation of a tetracyclic β-lactonic acid, but to the more stable, hexacyclic o-lactonic derivative, carboxycoumarin. On the other hand, cinnamic aldehyde reacts with malonic acid by the Meldrum method to form cinnamalmalonic acid, which partially condenses, at the carboxyl groups, with the aldehyde to give the corresponding acetal derivative.

2. The thermal and chemical properties of β-lactonic acids and their alkali salts have been further examined, and it has been shown that all the compounds are cleaved by heat, and by alkali, through the first-formed β-hydroxy malonates, by rupture at the α,β-carbon linkage. The contradicting statements of Khandiah, and assumption of Salkowski[5] have been disproved.

CAMBRIDGE, MASS. RECEIVED JANUARY 31, 1936

[CONTRIBUTION FROM THE PATHOLOGICAL DIVISION, BUREAU OF ANIMAL INDUSTRY]

Deltaline, A New Alkaloid from *Delphinium Occidentale* S. Wats

BY JAMES FITTON COUCH

The larkspurs form a genus of important stock-poisoning plants on the western ranges and in the southern Appalachian mountains. *Delphinium occidentale* is less toxic than the more important *D. barbeyi* which it closely resembles and with which it grows over a wide area of the western mountains. The toxic properties of *D. scopulorum* have been ascribed by Heyl[1] to an amorphous alkaloid melting at 184–185° which he named delphocurarine and assigned the formula $C_{23}H_{33}O_7N$. It was of interest to determine whether the less toxic *D. occidentale* contains the same substance in smaller amounts or some other less poisonous base.

Examination of a quantity of the whole plant of *D. occidentale* collected in Utah has resulted in the isolation of a crystalline alkaloid to which the name deltaline has been assigned in accordance with the system first used by Markwood.[2] This substance has the empirical formula $C_{21}H_{33}O_6N$ and is therefore isomeric with one of the alkaloids,

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(1) G. Heyl, *Süddeut. Apoth.-Ztg.*, **43**, 249–51 (1903).

(2) Markwood, *J. Am. Pharm. Assoc.*, **13**, 696–702 (1924).