contained a small amount of metallic selenium which cleaved as selenide during the hydrolysis. After cooling, the crystals were filtered off, washed with ethanol to remove any unhydrolyzed hydantoin and dried. The yield of crude product was 56 g., 90% of the theoretical.

The crude α-amino-γ-(benzylseleno)-butyric acid was dissolved in 500 ml. of hot water by adding excess hydrochloric acid, clarified with a little carbon, and filtered hot. The compound was precipitated by adjusting the *p*H to 5.5 and cooling. The yield of a compound decomposing at 250° was 52.7 g.

Anal. Calcd. for $C_{11}H_{15}NO_2Se$: N, 5.15; Se, 29.01. Found: N, 5.09; Se, 28.9.

The amino acid, α-amino-γ-(benzylseleno)-butyric acid synthesized by this method has been used to prepare the selenium analogs of methionine and homocystine.[3] By the addition of methyl iodide in the ratio of two moles to one of α-amino-γ-(benzylseleno)-butyric acid after the latter compound was reduced with sodium in liquid ammonia, the selenium analog of methionine was obtained in 80% yields.

Acknowledgment.—A generous supply of γ-butyrolactone from the Cliffs Dow Chemical Co., Midland, Michigan is gratefully acknowledged.

Summary

The compound 5-(β-bromoethyl)-hydantoin was treated with sodium benzyl selenide in ethanol to give 5-(β-benzylselenoethyl)-hydantoin. Hydrolysis of the latter with sodium hydroxide gave α-amino-γ-(benzylseleno)-butyric acid. Reduction of this amino acid with sodium in liquid ammonia yielded the selenium analog of homocysteine; by methylation of the reduced form the selenium analog of methionine is obtained.

DAVIS, CALIFORNIA RECEIVED MARCH 22, 1947

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL]

The Alkaloids of *Delphinium Consolida* L.[1]

BY LÉO MARION AND O. E. EDWARDS

As the number of investigations concerning the alkaloids of *Delphinium* species increases, it becomes evident that lycoctonine is of widespread occurrence. Lycoctonine, first found in *Aconitum lycoctonum* L.,[2] has been reported as occurring in *D. Brownii*,[3] *D. elatum* L.[4] and *D. ajacis* L.[5] and it has now been found in *D. consolida* L. in which it is one of the two major alkaloids. Although lycoctonine can be found in the free state it is generally esterified with anthranilic acid. This acid in turn is mostly always combined in the form of an amide with another acid which in the instances known is one of succinic acid,[2] methylsuccinic acid[3,4] or acetic acid.[5] In the present occurrence, however, lycoctonine itself has been isolated as well as anthranoyllycoctonine uncombined with another acid.

The seeds of *D. consolida* L. have been the subject of several contributions. Markwood[6] isolated two alkaloids which he designated delsoline and delcosine and reported the presence of a third crystalline alkaloid for which he gave no analytical figures. Recently, Cionga and Iliescu[7] confirmed the presence of delsoline and delcosine but failed to detect Markwood's third alkaloid. They rejected Markwood's empirical formulas and claimed that the two alkaloids are isomeric, putting forward the obviously incorrect formula $C_{25}H_{40}O_7N$ to represent them.

Besides delsoline and delcosine, the present investigation has revealed the presence of four more alkaloids in the seeds of *D. consolida*. These are lycoctonine, which is the most abundant, anthranoyllycoctonine and two new bases for which the names delsonine and consolidine are suggested. Although delsonine yields a crystalline perchlorate, the base itself is amorphous, but in the presence of boiling alcoholic potassium hydroxide it is converted into a crystalline, apparently isomeric, base which it is suggested to designate as isodelsonine. The last remaining base, consolidine, appears from its melting point to be probably identical with Markwood's third base.[6] When hydrolyzed, consolidine gives rise to one mole of benzoic acid and an amorphous base.

From the previously known delsoline and delcosine and from their salts, analytical figures have been obtained which do not support the claim of Cionga and Iliescu[7] that the two bases are isomeric. The analytical data are in best agreement with the empirical formulas $C_{25}H_{43}O_7N$ for delsoline and $C_{22}H_{37}O_6N$ for delcosine. The formula of delsoline can be expanded to $C_{21}H_{31}O_3N(OCH_3)_4$ and that of delcosine to $C_{19}H_{25}N(OH)_3(OCH_3)_3$. The latter differs by CH_4 from the formula suggested by Markwood[6] for delcosine. Furthermore, whereas Cionga and Iliescu[7] reported the two bases to be levorotatory, we found that although the figures expressing the optical activities are in good agreement with theirs, both delsoline and delcosine are dextrorotatory.

Delcosine absorbed one mole of bromine but the compound formed appeared to be of the nature of a perbromide. When delcosine was acetylated it gave rise to a mixture of two derivatives. The most abundant of the two yielded analytical figures in good agreement with those required by triacetyldelcosine whereas the other appeared to be a compound derived from triacetyldelcosine by

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[1] Published as National Research Council Bull. No. 1442.

[2] H. Schulze and E. Bierling, *Arch. Pharm.*, **251**, 8 (1913).

[3] L. Marion and R. H. F. Manske, *Can. J. Research*, **B24**, 1 (1946).

[4] J. A. Goodson, *J. Chem. Soc.*, 139 (1943).

[5] J. A. Goodson, *ibid.*, 108 (1944).

[6] L. N. Markwood, *J. Am. Pharm. Assoc.*, **13**, 696 (1924).

[7] E. Cionga and C. Iliescu, *Ber.*, **74**, 1031 (1941).

the loss of one mole of acetic acid. The loss of acetic acid has already been observed in the so-called pyrolysis of aconite alkaloids and their acetyl derivatives.[8]

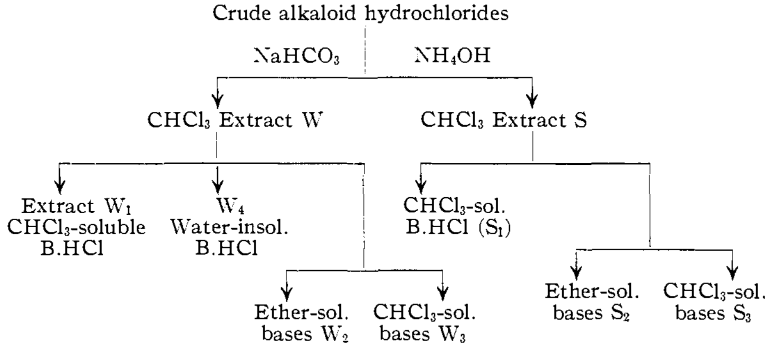
Experimental

The crushed seed of *Delphinium consolida* L. (22.7 kilograms, obtained from City Chemical Corporation, N.Y.) was extracted in Soxhlets with methanol. The combined extract which contained a large layer of fat was stirred with sufficient methanolic oxalic acid to give an acid reaction to congo and repeatedly extracted with petroleum ether (30–60°). The petroleum ether extract was washed with 80% methanol containing oxalic acid and the washings added to the main methanolic solution. Most of the methanol in the defatted solution was then distilled off under reduced pressure and the residual sirup diluted with water and filtered. The filtrate was repeatedly extracted with ether, basified with ammonium hydroxide and exhaustively extracted with chloroform. The chloroform was distilled from the combined extract and the residual basic material dissolved in $3N$ hydrochloric acid. The aqueous acid solution was repeatedly extracted with ether, the bases precipitated with ammonia and collected in chloroform. After removal of the chloroform by distillation the crude basic residue weighed 285 g.

The crude alkaloid was dissolved in the minimum quantity of $3N$ hydrochloric acid, the solution treated with an excess of aqueous sodium bicarbonate and thoroughly extracted with chloroform (extract W). The solution was then basified with an excess of ammonia and again exhaustively extracted with chloroform (extract S).

Chloroform extract W, containing the weak bases, was extracted with N hydrochloric acid, leaving in the chloroform the bases forming hydrochlorides soluble in that solvent (W_1). The aqueous solution was basified with ammonium hydroxide and extracted thoroughly first with ether (W_2) and subsequently with chloroform (W_3). During the shaking of extract W with acid a water-insoluble base hydrochloride separated. This was filtered and kept separately (W_4).

The chloroform extract S when treated similarly yielded the corresponding extracts S_1, S_2 and S_3. The method of separation is outlined in the following scheme



The chloroform solution W_1 was distilled to dryness but the residue (5.5 g.) failed to yield any crystallizable alkaloid or salt. The chloroform extract W_3 was evaporated to dryness and the residual gum dissolved in dilute hydrochloric acid. The solution was filtered and the filtrate basified with ammonia and extracted with chloroform. When evaporated to dryness the chloroform solution left a brown fluorescent gum, wt. 110 g.

Delcosine.—The fluorescent gum was dissolved in hot methanol and about one-tenth of the solution separated and diluted with water. This caused the precipitation of a gum which was filtered out and the filtrate was extracted with chloroform. The chloroform extract was evaporated to dryness, the residue dissolved in methanol and the solution made just acid to congo by the careful addition of 65% perchloric acid. A crystalline perchlorate began to separate almost immediately. It was filtered, dissolved in aqueous methanol, the solution basified with ammonia and extracted with chloroform. The residue left after evaporation of this chloroform extract was dissolved in methanol and the solution on standing deposited a crystalline base. These crystals were used to seed the main methanol solution which after a few days had deposited a voluminous crystalline precipitate. The filtered crystalline base was recrystallized twice from methanol–ether, from which it separated as beautiful, colorless, hexagonal prisms melting at 203–204°[9] when immersed in the bath at 190°, wt. 32 g. It is quite soluble in water, $[\alpha]^{25}\mathrm{D}$ +56.8° (c = 2.01 in chloroform). This base seems to be the delcosine of Markwood[6] and Cionga and Iliescu.[7]

Anal. Found: C, 64.07, 63.93; H, 9.14, 8.92; N, 3.28, 3.28, 3.45, 3.34; OCH_3, 20.97, 22.08; mol. wt. (by isothermal distillation against azoxybenzene in chloroform), 425. Calcd. for $C_{22}H_{37}O_6N$: C, 64.24; H, 9.00; N, 3.41; 3 OCH_3, 22.63; mol. wt., 411.

Delcosine Perchlorate.—A small quantity of delcosine was dissolved in methanol and the solution neutralized with 65% perchloric acid. The perchlorate which crystallized was filtered and recrystallized from methanol from which it was obtained as colorless, triangular plates, melting at 217–218° when immersed at 195°, $[\alpha]\mathrm{D}$ +32.0° (c = 2.00 in dry methanol).

Anal. Found: C, 52.36, 52.34; H, 7.53, 7.07; N, 2.50, 2.51. Calcd. for $C_{22}H_{37}O_6N \cdot HClO_4$: C, 51.62; H, 7.43, N, 2.74.

Delcosine Hydrobromide.—A small quantity of delcosine (0.1 g.) was dissolved in methanol and the solution made just acid to congo by the dropwise addition of hydrobromic acid previously diluted with methanol. The resulting solution was evaporated down almost to dryness, the residue dissolved in a small volume of acetone and ether was then added to the point of incipient turbidity. The hydrobromide separated as colorless, silky needles which after one recrystallization from acetone–methanol began to shrink at 98° and melted at 103° (dec.).

Anal. Found: C, 51.19, 51.02; H, 8.16, 8.06; N, 2.54, 2.58. Calcd. for $C_{22}H_{37}O_6N \cdot HBr \cdot 2CH_3OH$: C, 51.80; H, 8.27; N, 2.52.

Delcosine Hydrochloride.—When a solution of delcosine in methanol was made just acid to congo by the dropwise addition of hydrochloric acid previously diluted with methanol and the solution treated as described for the hydrobromide, delcosine hydrochloride was obtained as small warts which first appear transparent and become white, shrink at 85° and melt at 89°.

Anal. Found: C, 56.99, 56.71; H, 8.93, 8.69; N, 2.33, 2.40. Calcd. for $C_{22}H_{37}O_6N \cdot HCl \cdot 2CH_3OH$: C, 56.31; H, 9.00; N, 2.74.

Delcosine when refluxed with alcoholic potassium hydroxide was not saponified and unchanged delcosine was recovered.

Acetylation of Delcosine.—Delcosine (0.7 g.) was refluxed for two and one-half hours with acetyl chloride (4 g.) during which time the base dissolved gradually. The excess acetyl chloride was distilled off, the residue dissolved in water and the solution basified with sodium carbonate. The precipitated acetyl derivative was extracted with chloroform, the extract deprived of solvent by distillation and the residue dissolved in methanol. On standing, crystals were deposited which after two recrystallizations from methanol were obtained as colorless rectangular plates melting at 203° (dec.) when immersed at 170°, wt. 0.11 g.

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(8) L. Marion and O. E. Edwards, THIS JOURNAL, **68**, 2565 (1946).

(9) All melting points are corrected.

Anal. Found: C, 62.77, 62.62; H, 8.29, 8.32. Calcd. for $C_{22}H_{34}O_6N(COCH_3)_3$: C, 62.56; H, 8.01.

The mother liquor from which the foregoing acetyl-derivative had crystallized was concentrated under reduced pressure. An oil separated which gradually crystallized, wt. 0.55 g., m. p. 142–154°. After four recrystallizations from aqueous methanol and one from ether–petroleum ether from which it separated as rectangular prisms or plates it melted at 157–161° when immersed at 147°. In admixture with the acetyl derivative of m. p. 203° it melted at 147–172°.

Anal. Found: C, 64.97, 64.85; H, 8.35, 8.52. Calcd. for $C_{22}H_{33}O_5N(COCH_3)_2$: C, 65.42; H, 8.18.

Treatment of Delcosine with Bromine.—To a chloroform solution of delcosine, a solution made up of a weighed quantity of bromine in chloroform (10 cc.) was added dropwise until the color caused by one drop persisted for five minutes. Titration of the excess bromine solution showed that delcosine had absorbed one mole of bromine. The solution containing the brominated delcosine was evaporated to dryness under reduced pressure, the residual gum dissolved in dilute hydrochloric acid and the solution basified with sodium carbonate. The bromo derivative which precipitated was crystallized from methanol from which it separated as diamond-shaped plates, which sinter at 197° and melt at 202°. When this compound was redissolved in methanol and the solution concentrated, delcosine crystallized out as hexagonal prisms, m. p. 203–204° alone or after admixture with pure delcosine. The mother liquor when allowed to concentrate by spontaneous evaporation, deposited a small quantity of the diamond-shaped plates. Cionga and Iliescu[7] claimed that the absorption of one mole of bromine by delcosine was evidence of the presence of a double-bond in the alkaloid. The behavior of the bromo derivative, however, which precipitated silver bromide from an aqueous solution of silver nitrate and liberated iodine from a potassium iodide solution is indicative of a perbromide rather than a dibromo-addition compound.

Delsoline.—The methanolic mother liquor from which the bulk of the delcosine had crystallized was neutralized by the cautious addition of 65% perchloric acid. On standing some delcosine perchlorate crystallized which was filtered out. The filtrate was diluted with an equal part of water which caused the precipitation of a gum from which the supernatant liquor was decanted. This liquor was basified with ammonia and the liberated base collected in chloroform. The volume of 0.5 *N* sulfuric acid necessary to neutralize the base was divided into three portions and the chloroform solution shaken with each portion. The first portion was basified with ammonia and the liberated base converted to perchlorate. It yielded lycoctonine perchlorate (see below). The second portion yielded a further quantity of delcosine. The third portion when basified with ammonia gave a mixture of bases part of which was soluble in ether. The ether was distilled off and the residue dissolved in hot methanol. On standing, this solution deposited a crystalline base which after recrystallization from methanol was obtained as colorless, complex prisms melting at 213–216.5° when immersed at 205°, $[\alpha]^{28}\text{D}$ +51.7° (c = 2.09 in chloroform), wt. 2 g.

Anal. Found: C, 64.27, 64.10; H, 9.03, 8.95; N, 3.05, 3.19; OCH_3, 26.13, 25.97. Calcd. for $C_{25}H_{43}O_7N$: C, 63.97; H, 9.17; N, 2.99; $4OCH_3$, 26.43.

From its melting point, analysis and behavior, this base appears to be identical with the delsoline of Markwood[6] and Cionga and Iliescu.[7] The perchlorate of delsoline separated from a concentrated methanolic solution after the addition of absolute ether as colorless stout needles containing methanol of crystallization. This, however, is lost on standing and the crystals crumble to a white powder. The dry crystals melt at 192.5–193.5° (dec.) when immersed at 180°, $[\alpha]^{27}\text{D}$ +28.1°, (c = 1.73 in methanol).

Anal. Found: C, 52.41, 52.71; H, 7.46, 7.64. Calcd. for $C_{25}H_{43}O_7N \cdot HClO_4$: C, 52.68; H, 7.73.

Delsoline Hydrobromide.—A small quantity of delsoline was dissolved in a little methanol, the solution made just acid to congo with 45% hydrobromic acid and evaporated to dryness under reduced pressure. The residual hydrobromide was crystallized with difficulty from acetone from which it separated as colorless needles containing solvent of crystallization. It melted at 83°.

Anal. Found: N, 2.54, 2.68. Calcd. for $C_{25}H_{43}O_7N \cdot HBr \cdot 0.5C_3H_6O$: N, 2.42.

Delsoline is not hydrolyzable and even after refluxing for two hours with alcoholic potassium hydroxide, the unchanged base is recovered.

Delsonine.—The ether extract W_2, when distilled to dryness, left a reddish brown gum exhibiting a strong bluish fluorescence, wt. 110 g. It was dissolved in chloroform (150 cc.) and fractionated by extracting the solution with nine 33-cc. portions of *N* sulfuric acid. Fraction 1 yielded a further quantity of lycoctonine. Fraction 2 when basified with ammonia deposited a gum which was separated and the aqueous solution extracted with chloroform. This chloroform extract yielded a further small quantity of delcosine. The gum which had separated on the addition of ammonia was dissolved in methanol and the solution made just acid to congo with 65% perchloric acid. On standing, a perchlorate crystallized which was filtered and recrystallized from methanol from which it separated as colorless, rectangular, flat prisms melting at 216° (dec.) when immersed at 205°, $[\alpha]^{32}\text{D}$ +23° (c = 0.412 in methanol).

Anal. Found: C, 53.51, 53.69; H. 7.82, 8.06; N, 2.57, 2.54; Cl, 5.88, 6.30; OCH_3, 25.75, 25.76. Calcd. for $C_{24}H_{41}O_6N \cdot HClO_4$: C, 53.58; H, 7.78; N, 2.59; Cl, 6.58; $4OCH_3$, 22.98; $5OCH_3$, 28.72.

It is suggested that this base be designated delsonine. The perchlorate of delsonine was dissolved in hot water, the solution cooled, basified with ammonia and extracted with chloroform. All attempts to crystallize the base, however, failed. A small quantity of the free base was dissolved in methanol and the solution neutralized with hydriodic acid of constant boiling point. The solution was concentrated to a small volume and absolute ether added dropwise to incipient turbidity. Delsonine hydriodide separated as clusters of colorless six-sided plates. After recrystallization from methanol–ether it melted at 202°.

Anal. Found: C, 50.93, 51.07; H, 7.51, 7.69. Calcd. for $C_{24}H_{41}O_6N \cdot HI$: C, 50.79; H, 7.41.

Amorphous delsonine (0.160 g.) was refluxed for two hours with alcoholic potassium hydroxide, the solution evaporated to dryness and the residue warmed with water and extracted with chloroform. The aqueous solution was then acidified with hydrochloric acid and repeatedly extracted with ether. This last extract yielded only a trace of a gum (15 mg.) which did not distil at 220° (0.5 mm.). The chloroform extract containing the base was evaporated to dryness and the residue which was very soluble in both methanol and ether was crystallized from aqueous methanol and recrystallized from the same solvent. It consisted of small colorless elongated prisms melting at 108–111°. It is proposed to designate this base which is isomeric with delsonine as isodelsonine.

Anal. Found: C, 65.15, 65.27; H, 9.02, 8.94; N, 4.02; OCH_3, 32.89, 32.22. Calcd. for $C_{24}H_{41}O_6N$: C, 65.60; H, 9.34; N, 3.18; $4OCH_3$, 28.24; $5OCH_3$, 35.30.

Delsonine perchlorate was also obtained from fraction 8 of extract W_2.

Consolidine.—The methanolic mother liquor from which delsonine perchlorate had crystallized was concentrated to about half-volume and allowed to cool and stand. It deposited a perchlorate which, after recrystallization from methanol, consisted of colorless wedge-shaped prisms melting at 252° when immersed at 240°, $[\alpha]^{28}\text{D}$ +33° (c = 0.589 in 90% methanol).

Anal. Found: C, 56.54, 56.11, 56.22; H, 7.08, 7.08, 6.98; N, 1.91, 2.10; Cl, 4.88, 4.78. Calcd. for $C_{33}H_{49}O_9N \cdot HClO_4$: C, 56.29; H, 7.11, N, 1.99; Cl, 5.05.

The perchlorate was dissolved in hot water, the solution cooled quickly, basified with ammonia and extracted with chloroform. The residual gum was dissolved in hot methanol and the solution on standing deposited a crystalline base. After several recrystallizations from methanol it was obtained as colorless, prismatic needles melting at 153–157° when immersed at 145°, $[\alpha]_D$ +64° (c = 0.360 g. in methanol). It is proposed to name this base consolidine. It likely corresponds to Markwood's third base (m. p. 153–160°) for which he reported no analytical figures.

Anal. Found: C, 65.12, 65.27; H, 8.10, 8.29; N, 2.96, 2.87; OCH_3, 17.64, 17.16. Calcd. for $C_{33}H_{49}O_9N$: C, 65.67; H, 8.13; N, 2.32; $3OCH_3$, 15.43; $4OCH_3$, 20.56.

A small quantity of consolidine was refluxed for two hours with methanolic potassium hydroxide and the solution subsequently evaporated to dryness. The residue was shaken with a mixture of chloroform and water, the chloroform separated, the aqueous solution acidified with hydrochloric acid and extracted with ether. The dried ether extract when concentrated to a small volume and diluted with petroleum ether deposited a crystalline acid which after recrystallization from ether–petroleum ether melted at 122° either alone or after admixture with benzoic acid. The chloroform extract yielded the hydrolytic base which could not be induced to crystallize either as such or in the form of its perchlorate. The name consoline is suggested to designate the hydrolytic base obtained from consolidine.

Anthranoyllycoctonine.—Fractions 3 and 4 of the extract W_2 were basified with ammonia. In each case this caused the precipitation of a gum from which the supernatant liquor was decanted. The decantate from fraction 3 yielded a little delcosine while the decantate from fraction 4 yielded a little delsoline. The gums which had separated were combined, dissolved in methanol and the solution neutralized with 65% perchloric acid. A perchlorate crystallized out which when recrystallized from methanol consisted of colorless rectangular plates, m. p. 207°; $[\alpha]_D$ +29.3° (c = 0.784 in 90% methanol), wt. 28 g.

Anal. Found: C, 55.14, 54.96, 55.68; H, 7.18, 7.31, 7.93; N, 3.44, 3.48, 3.74; Cl, 5.40, 5.21. Calcd. for $C_{27}H_{38}O_6N_2 \cdot HClO_4$: C, 55.24; H, 6.65; N, 4.77; Cl, 6.05.[10]

The base liberated from the perchlorate was a faintly yellow gum which could not be induced to crystallize. Its solutions exhibited a strong blue fluorescence, $[\alpha]_D$ +54° (c = 1.930 in absolute methanol). A solution of the base hydrochloride in slightly acid water had $[\alpha]_D$ +24° (c = 1.131). Goodson[4] gives $[\alpha]^{24}_D$ +32.4° (c = 2 in 0.2N hydrochloric acid) and m. p. 172° for his crystalline anthranoyllycoctonine. The amorphous base dissolved in methanol and neutralized with hydriodic acid gave rise to a hydriodide which separated from methanol as flat, pale yellow needles melting at 183° when immersed at 172° $[\alpha]_D$ +33° (c = 0.550 in methanol).

Anal. Found: C, 51.89, 51.98, 52.55; H, 7.10, 7.21, 7.31. Calcd. for $C_{27}H_{38}O_6N_2 \cdot HI$: C, 52.77; H, 6.35.

Although the base could be crystallized in the form of its salts only, it is an anthranoyllycoctonine either identical or isomeric with the crystalline anthranoyllycoctonine reported by Goodson since,[4] when hydrolyzed with alcoholic potassium hydroxide, it gives rise to lycoctonine and anthranilic acid. The hydrolysis liquor was evaporated to dryness and the residue taken up in water and thoroughly extracted with chloroform. The chloroform extract was washed with water, evaporated to dryness and the residual gummy base crystallized from aqueous methanol from which it separated as colorless needles which sinter at 125° and melt at 135° either alone or in admixture with lycoctonine. The basic solution which had been extracted with chloroform was brought to pH 6 with sulfuric acid and extracted with ether. The combined ether extract was distilled to dryness and the dark residue distilled *in vacuo*. The acid sublimed at 120–130° (0.4 mm.). It was crystallized from ether–petroleum ether from which it separated as colorless needles, m. p. 147° either alone or in admixture with an authentic sample of anthranilic acid.

Furthermore, acid hydrolysis of the base, by the procedure used by Goodson[5] for converting ajacine into anthranoyllycoctonine, failed to alter it since it could be converted to the same perchlorate m. p. 207° that it yielded originally. The base appears to be isomeric rather than identical with Goodson's crystalline anthranoyllycoctonine since all attempts to crystallize it failed and since the optical rotation is different from that reported by Goodson.

The mother liquor from which anthranoyllycoctonine perchlorate had separated was concentrated and allowed to stand. It gradually deposited a small quantity of consolidine perchlorate.

Fractions 5, 6 and 7 obtained by fractionation of the ether extract W_2 were treated as fractions 3 and 4. Each yielded more anthranoyllycoctonine and a little delsoline. The mother liquors from all fractions were combined, reconverted to base, dissolved in chloroform and again fractionated by shaking with ten fractions of 0.5N sulfuric acid. These new fractions yielded further small quantities of the alkaloids obtained in the first fractionation.

In all cases, a weight reported is the total weight of that alkaloid isolated.

Lycoctonine.—When extract S_1 containing the chloroform-soluble hydrochlorides of the strong bases was worked up, it yielded only a small quantity (1 g.) of a gum which could not be crystallized. The extract S_2 when evaporated left a clear yellow gum which was dissolved in 90% methanol. The solution while standing overnight deposited a crystalline base which after recrystallization from 90% methanol from which it separated as colorless needles, began to fuse at 125° and melted at 135°. Extract S_3, when worked up similarly yielded a crop of the same base, total wt. 36 g. Admixture of this base with an authentic sample of lycoctonine[3] did not lower the melting point. A small quantity of the base was dissolved in methanol and the solution made just acid to congo by the cautious addition of 65% perchloric acid. The dropwise addition of absolute ether to the solution caused the separation of the crystalline perchlorate. After recrystallization from methanol–ether from which it separated as colorless prisms it melted at 208° (dec.) when immersed at 190°. In admixture with lycoctonine perchlorate (m. p. 213°) it melted at 210°. The methiodide prepared by heating a methanolic solution of the base with methyl iodide for one hour at 100° in a sealed tube was recrystallized from a mixture of methanol and ethyl acetate. It melted at 172° either alone or after admixture with lycoctonine methiodide.

Summary

1. The seeds of *Delphinium consolida* L. have been investigated and found to contain at least six alkaloids. The alkaloids which crystallized either as base or in the form of salts represented one-third of the total crude alkaloid.

2. The three main alkaloids are lycoctonine, delcosine and anthranoyllycoctonine, while the others are delsoline, delsonine and consolidine.

3. Delcosine is a non-hydrolyzable base which yields salts, a perbromide and two acetyl derivatives.

4. Delsoline and delsonine are non-hydrolyzable bases, but the latter which is amorphous is

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(10) Lycoctonine, its salts and derivatives are extremely difficult to analyze for nitrogen. Its empirical formula is uncertain and it will be possible to determine it accurately only after simpler degradation products have been prepared from the alkaloid. The formula used here for anthranoyllycoctonine is based on that suggested by Marion and Manske[3] for lycoctonine.

converted to a crystalline isomer when heated with alcoholic potassium hydroxide.

5. Consolidine is a crystalline base which can be hydrolyzed to benzoic acid and amorphous consoline.

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[JOINT CONTRIBUTION FROM THE KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY, WITH THE CALIFORNIA FOREST AND RANGE EXPERIMENT STATION[1]]

Composition of Gum Turpentine of Torrey Pine

BY A. J. HAAGEN-SMIT, C. T. REDEMANN AND N. T. MIROV

The Torrey pine (*Pinus torreyana* Parry) is an endemic California pine found naturally only in two places: one, near La Jolla, California; the other, on Santa Rosa Island, California. It is occasionally planted in parks in California.

Botanically, the Torrey pine is related to the Coulter pine (*Pinus coulteri*) and the Digger pine (*Pinus sabiniana*); these pines form the morphologically distinct group *Macrocarpae*.

The composition of turpentine of Digger pine and of Coulter pine has been determined by previous investigators. It was found that Coulter pine turpentine is composed of *l*-α-pinene, and *l*-β-phellandrene, together with the paraffin hydrocarbons *n*-undecane and *n*-heptane.[2] Similarly, the paraffin hydrocarbon *n*-heptane occurs in Digger pine turpentine to the extent of 95%[3]; the remaining 5% consists of normal saturated aldehydes.[4]

As most pines produce turpentine composed of terpenes, the paraffin hydrocarbons being found only in a few species, it appeared interesting to investigate the chemistry of the turpentines from this third pine of the *Macrocarpae*.

Conventional methods of chemical investigation revealed that Torrey pine turpentine consists of 75% *l*-limonene, together with 4% sesquiterpene, longifolene, 10% *n*-decyl aldehyde, 0.2% lauryl aldehyde, 0.2% of an unidentified C_{10} carbonyl compound, and 5% *n*-undecane.

Mass distribution analysis of suitably purified fractions performed on a Consolidated Engineering[5] mass spectrometer confirmed the presence of *n*-undecane and revealed the presence of minute amounts of compounds having masses equal to those of nonane and *n*-heptane.

Although we could readily detect the presence of aldehydes containing an even number of carbon atoms in the molecule and of paraffins containing an odd number of carbon atoms, we were unable to detect aldehydes having an odd number of carbon atoms, or more than the minutest trace of a paraffin with an even number of carbon atoms. We feel that this observation may bear considerable significance relative to the bio-synthesis of paraffin hydrocarbons by the pines.

Experimental

Collection of Oleoresin.—About 4,000 g. of oleoresin was collected from three planted trees, about forty years old, growing in Golden Gate Park, San Francisco, California. Conventional turpentining methods were used; the trees were tapped once a week, and the oleoresin was collected also once a week. The tapping was started in May and discontinued in October. There was no difference in the yield of oleoresin throughout the summer; each tree yielded between 2.5 and 3 ounces per streak.

Separation of Turpentine from Rosin.—The volatile oil was expelled from oleoresin by heating it under vacuum, bringing the bath temperature to 200° and the pressure to 0.01 mm. There was no appreciable difference in the yield of volatile oil in the oleoresin samples obtained during different months of the operation; neither was there any difference in the yield of the oil by the three trees. The average figures, based on distillation of 17 batches of oleoresin were as follows

Volatile oil (turpentine)	17.1%
Rosin	81.9
Water	1.0

Physical Constants of Turpentine.—The turpentine samples obtained from the three trees at the different months of the season were analyzed with respect to their physical properties: density, index of refraction and optical rotation. These values showed no distinct trend with respect to time of collection of the oleroresin, nor did they vary greatly from tree to tree.

The maximum observed values of density, $d^{23.5}_{4}$, index of refraction, $n^{25}\text{D}$, and specific rotation, $[\alpha]^{25}\text{D}$, were 0.8366, 1.4660 and −121.95°, respectively. The minima were 0.8355, 1.4650 and −115.47°.

The composite turpentine sample with which this paper deals had for $d^{23.5}_{4}$, $n^{25}\text{D}$ and $[\alpha]^{25}\text{D}$ the values 0.8360, 1.4656 and −118.12°, respectively.

Fractional Distillation of Turpentine.—A batch of 300 g. of Torrey pine turpentine was fractionated into 20 parts by distillation through a 12-inch column packed with glass helices, surrounded by a heating jacket, and provided with a constant reflux ratio still-head. The 20 g. of residue was then separated into an additional 5 fractions by distillation through a 4-inch Vigreux column equipped with a variable take-off still-head.

The results of this fractionation are tabulated in Table I.

Preparation of Low-boiling Fractions for Mass Spectroscopy.—The low densities and refractive indices of the lower-boiling fractions indicated the presence of compounds other than terpene hydrocarbons. A micro analysis[6] of Fraction 1, however, showed a composition of 12.47%

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(1) Maintained by the Forest Service, U. S. Department of Agriculture, in coöperation with the University of California.

(2) Mirov, *Ind. Eng. Chem.*, **38**, 405–408 (1946).

(3) Schorger, "An Examination of the Oleoresins of Some Western Pines," *U. S. Dept. Agr. Forest Serv. Bull.*, 119 (1913).

(4) Uhl, *J. Am. Pharm. Assoc.*, **24**, 380 (1935).

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