was partially filled with water and ice and located one floor-level below. After a short period of stirring, the hydrocarbon layer was removed and worked up as in the previous procedure. Final purification was effected by a second fractionation of the individual isomers accumulated from both syntheses.

o-t-Butyltoluene.—The Grignard reagent was made using 85 moles of magnesium covered with 12 liters of dry ether to which was added over a period of five hours 80 moles of *o*-bromotoluene (f.p. −26.91° and $n^{20}D$ 1.5563) dissolved in 5 liters of dry ether. This was condensed with 72 moles of *t*-butyl chloride dissolved in 5 liters of dry ether and the reaction mixture was stirred overnight. After hydrolysis with dilute hydrochloric acid, the hydrocarbon layer was separated and the ether was evaporated.

The crude product was then dried over sodium sulfate and fractionated on a 15-theoretical plate column. Halogen impurities were removed by treatment with sodium in liquid ammonia. It was finally fractionated on a six-foot Podbielniak column and the yield of pure hydrocarbon based on the *t*-butyl chloride is shown in Table I.

Oxidation of *t*-Butyltoluenes.—No difficulty was encountered in the oxidation of the *m*- and *p*-isomers. The *t*-butylbenzoic acids obtained by the alkaline-permanganate method were found to be identical with those obtained by dilute nitric acid oxidation after maximum purity was attained by successive recrystallizations out of ethyl alcohol. Several attempted oxidations of the *o*-isomer using alkaline permanganate resulted in an oil which could not be crystallized. When the oil was purified by distillation at reduced pressure, a solid product was obtained which was recrystallized out of neohexane and found upon analysis to be *o-t*-butylbenzoic acid. The data on these acids are shown in Table II.

The oxidation of *o-t*-butyltoluene was also carried out in a sealed tube using dilute nitric acid and heating at 170° for twelve hours. Phthalic acid was precipitated out by the addition of chloroform to the oil resulting in this procedure and this was sublimed to phthalic anhydride, which gave no depression in melting point when mixed with an authentic sample (m.p. 130.8°).

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Summary

1. The use of boron trifluoride as an alkylation catalyst has been shown to result in mixtures of *p*- and *m-t*-butyltoluenes in the reaction between toluene and *t*-butyl alcohol. The yield of each isomer is nearly the same but when aluminum chloride is used as the catalyst the *m*-isomer is appreciably greater with a corresponding decrease in yield of the *p*-compound.

2. The preparation and characterization of *o-t*-butyltoluene has been described. The physical properties have been shown to differ from those reported in the only earlier work on the synthesis of this hydrocarbon.

3. The physical properties of the three isomeric *t*-butyltoluenes in high purity have been described and time-temperature freezing or melting curves for these compounds are shown.

4. The oxidation of *o*-, *m*- and *p-t*-butyltoluenes to the corresponding *t*-butylbenzoic acids has been described and *o-t*-butylbenzoic acid has been reported for the first time.

5. Partial infrared absorption data for the *t*-butyltoluenes have been determined for purposes of gross structural analysis and the data have been shown to be in good agreement with previous work wherein characteristic absorption spectra for disubstituted aromatic compounds have been evaluated.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK & CO., INC.]

Erythrina Alkaloids. XVI. Studies on the Constitution of Erysodine, Erysovine and Erysopine[1]

BY FRANK KONIUSZY, PAUL F. WILEY AND KARL FOLKERS

Structure studies on erysodine, erysovine and erysopine have elucidated the functional groups and the number of rings of each alkaloid, and have shown that each has the same ring system.

These three *Erythrina* alkaloids[2,3,4] have interesting curare-like pharmacologic action.[5] Erysodine and erysovine have the same molecular formula, $C_{18}H_{21}NO_3$; each has two methoxyl groups and one phenolic hydroxyl group. Therefore, the functional groups containing all the oxygen atoms of erysodine and erysovine are known.[2] Erysopine[2] has the formula $C_{17}H_{19}NO_3$, one methoxyl group, and two phenolic hydroxyl groups which are ortho as indicated by a color reaction with ferric chloride. None of these three alkaloids showed the presence of an N-methyl group or a C-methyl group. The presence of methoxyl groups, and particularly the phenolic hydroxyl groups, implies the presence of at least one benzenoid nucleus in all three alkaloids.

A facile reaction between erysodine and methyl iodide to give the crystalline quaternary salt, erysodine methiodide, proved the tertiary nature of the nitrogen atom in erysodine.

Erysodine reacted with two molar equivalents of hydrogen with Adams platinum catalyst at atmospheric pressure. The ease of hydrogenation was

(1) Presented in part at the Meeting of the American Chemical Society in Atlantic City, N. J., September 10, 1941; Abstracts of Papers, Division of Organic Chemistry, p. 30.

(2) Folkers and Koniuszy, THIS JOURNAL, **62**, 1677 (1940).

(3) Gentile and Labriola, *J. Org. Chem.*, **7**, 136 (1942).

(4) Deulofeu, Labriola, Hug, Fondovila and Kauffman, *J. Org. Chem.*, **12**, 486 (1947).

(5) Unna and Greslin, *J. Pharmacol.*, **80**, 53 (1944).

typical of that of semi-saturated cyclic alkaloidal structures. The tetrahydroerysodine was isolated as a crystalline free base and hydrobromide. The fact that this hydrogenation reaction involved two >C=C< groups and not one >C=C< group and one >C=N— group was shown by the reaction of the tetrahydroerysodine with acetic anhydride to give crystalline O-acetyltetrahydroerysodine. The reduction of a >C=N— group to a >CH—NH— group would be expected to lead to an O-acetyl-N-acetyl derivative upon acetylation. On the basis of these data, the nitrogen atom of erysodine appears to be shared by two nuclei.

Erysopine was hydrogenated under similar conditions to give tetrahydroerysopine, which was isolated as a crystalline hydrobromide.

"Erysocine,"[6] which is a "complex" of erysodine and erysovine, absorbed two molar equivalents of hydrogen, similarly. The hydrogenation product yielded a crystalline tetrahydro-"erysocine" hydrobromide which did not separate into its components on crystallization.

It was observed[2] before that a characteristic property of erysodine, erysovine and erysopine is their weakly basic nature. For example, erysodine crystallizes from ethanol containing excess hydrogen chloride. Although erysodine dissolves in aqueous hydrochloric acid, it can be nearly completely removed by several chloroform extractions. Erysovine was converted into a crystalline hydrobromide and hydroiodide. Erysodine is also weakly acidic and could be removed from 2% aqueous sodium hydroxide solution by repeated chloroform extraction.

Since erysodine has two methoxyl groups, one phenolic hydroxyl group, a tertiary nitrogen atom shared by two nuclei, two "ethylenic" double bonds, and a benzenoid nucleus, it is now evident that erysodine has four nuclei in its ring system.

It appeared probable that erysodine, erysovine and erysopine have the same ring system, that the three oxygen atoms of each are in the same position and that each differs in the position or number of the O-methyl groups. This relationship between the alkaloids was investigated by methylation reactions.

Erysodine and erysopine reacted with dimethyl sulfate in alkaline aqueous solution to give identical crystalline products of the formula $C_{21}H_{29}NO_7S$. This composition corresponds to the methomethylsulfate of O-methylerysodine and O-dimethylerysopine, respectively. For simplicity of nomenclature, the fully oxygen-methylated alkaloid is designated "erysotrine"; hence, this new product, $C_{21}H_{29}NO_7S$, is erysotrine methomethylsulfate. As other data prove, this product should also be produced from erysovine.

It was desirable to methylate the free phenolic hydroxyl group of these *Erythrina* alkaloids without methylating the tertiary nitrogen atom. The methylation of the phenolic hydroxyl groups of alkaloids by dimethyl sulfate is frequently accompanied by methylation of the nitrogen atom. Thus, the reaction of morphine with dimethyl sulfate in sodium hydroxide solution gave codeine methomethylsulfate.[7] To circumvent this difficulty, morphine was methylated by reaction with phenyltrimethylammonium hydroxide in alcohol at 110° and codeine was obtained.[8] Our experiments with this method, including several modifications, for the methylation of erysodine were not satisfactory. Tetramethylammonium hydroxide has been used[9] for methylating sterically hindered acids, but treatment of erysodine with this reagent was unsatisfactory. The result of treating erysodine with diazomethane was also unsatisfactory since much erysodine was recovered.

The nitrogen atom of morphine was "protected" in the methylation of morphine N-oxide; codeine was obtained by reduction of the oxide with sulfurous acid.[10] We have found that the N-oxides of these *Erythrina* alkaloids could be made readily and, after methylation, reduction with zinc dust and hydrochloric acid gave the fully oxygen-methylated tertiary alkaloid which could be extracted readily from an ammoniacal solution. It was shown separately that erysodine N-oxide could be reduced to erysodine with zinc and hydrochloric acid.

Treatment of erysodine N-oxide with dimethyl sulfate gave a non-crystalline erysotrine N-oxide which was reduced with zinc and hydrochloric acid to erysotrine. This fully oxygen-methylated tertiary base did not crystallize, but it did sublime *in vacuo* to give a gum of the expected composition, $C_{19}H_{23}NO_3$, and it gave a crystalline picrate. It may be that some erysotrine was produced in the above-mentioned unsatisfactory methylation experiments, but was not isolated because of its non-crystalline character.

Conversion of both erysovine and erysopine into their N-oxides, followed by methylation, reduction, and treatment with picric acid, gave crystalline picrates which were identical with the one derived from erysodine.

Erysonine[11] has the molecular formula $C_{17}H_{19}NO_3$, which is the same as that of erysopine. Erysonine does not give a green color with ferric chloride in aqueous solution as does erysopine showing that erysonine apparently does not have two ortho phenolic hydroxyl groups. The series of reactions used to obtain erysotrine picrate was applied to erysonine. Although 20 mg. of gummy product was obtained from 127 mg. of erysonine, it did not give a crystalline picrate even after additional manipulation and storage.

(6) Folkers and Shavel, THIS JOURNAL, **64**, 1892 (1942).

(7) Pschorr and Dickhäuser, *Ber.*, **44**, 2633 (1911); German Patent, 261,588 (1910), *Frdl.*, **11**, 989.

(8) Rodionov, *Bull. soc. chim.*, **39**, 305 (1926).

(9) Fuson, Corse and Horning, THIS JOURNAL, **61**, 1290 (1939).

(10) German Patent 418,391 (1923), *Frdl.*, **15**, 1515.

(11) Folkers, Shavel and Koniuszy, THIS JOURNAL, **63**, 1544 (1941).

The conversion of erysodine and erysopine into erysotrine methomethylsulfate, and the conversion of erysodine, erysovine and erysopine into erysotrine picrate prove that all three alkaloids have the same oxygenated ring system and differ only in the position or number of O-methyl groups. Furthermore, all three alkaloids have four nuclei in their ring system.

Experimental

Erysodine Methiodide.—A solution prepared from 150 mg. of erysodine, 1 ml. of methyl iodide, and 2 ml. of absolute methanol was refrigerated for twelve hours. The crystals, which were obtained, weighed 68 mg. and melted at 229–229.5°. Recrystallization of this product from 95% ethanol did not alter the melting point. The crystals were dried at 100° *in vacuo* for one hour.

Anal. Calcd. for $C_{18}H_{21}NO_3 \cdot CH_3I$: C, 51.70; H, 5.48; N, 3.18. Found: C, 51.82, 51.78; H, 5.62, 5.62; N, 3.27.

Tetrahydroerysodine.—A 508-mg. sample of erysodine was dissolved in 100 ml. of water to which 4 drops of concentrated hydrochloric acid had been previously added. The hydrogenation was carried out with 51 mg. of Adams platinum catalyst at atmospheric pressure and 2 moles of hydrogen was absorbed. After removal of the catalyst, the filtrate was made alkaline with sodium bicarbonate. The solution was extracted continuously with chloroform for eighteen hours. The chloroform extract was distilled under reduced pressure and 327 mg. of a gummy base was obtained; it crystallized after dissolving in 2 ml. of absolute ethanol. The crystals melted at 148–150°, and after three recrystallizations from ethanol, the melting point was constant at 152–153°. The tetrahydroerysodine was dried at 2 mm. and 25°.

Anal. Calcd. for $C_{18}H_{25}NO_3$: C, 71.25; H, 8.30; N, 4.61. Found: C, 71.10; H, 8.20; N, 4.78.

After a 2-g. sample of erysodine was hydrogenated, the chloroform residue of crude tetrahydroerysodine weighed 1.884 g. It was dissolved in 100 ml. of absolute ether and the solution was filtered to remove amorphous insoluble impurities. The filtrate was concentrated by distillation before crystallization, and 1.422 g. of tetrahydroerysodine was obtained; m. p. 150°. Recrystallization of this product from ether yielded crystals melting at 152–153° which is the same melting point observed for the product recrystallized from ethanol.

Tetrahydroerysodine Hydrobromide.—A 200-mg. sample of tetrahydroerysodine was dissolved in 2 ml. of absolute ethanol. After adding two drops of 40% aqueous hydrobromic acid, anhydrous ethyl ether (about ten drops) was added until incipient turbidity was observed. The crystals which were obtained melted at 247.5–248.5° and, after two recrystallizations from ethanol, the melting point was constant at 251–251.5° (dec.). The melting point was not changed by drying at 100° *in vacuo*.

Anal. Calcd. for $C_{18}H_{25}NO_3 \cdot HBr$: C, 56.25; H, 6.81. Found: C, 56.05; H, 6.65.

O-Acetyltetrahydroerysodine.—A 104-mg. sample of tetrahydroerysodine was added to 5 ml. of acetic anhydride and the solution was refluxed for ten minutes. After cooling, the solution was poured into 100 ml. of ice and water. When the excess anhydride had hydrolyzed, the solution was made alkaline with sodium bicarbonate and extracted six times with chloroform. Distillation of the chloroform extract yielded 109 mg. of colorless gum. A solution of this residue in 50 ml. of anhydrous ethyl ether was diluted with 5 ml. of petroleum ether, filtered, and concentrated to a volume of 12 ml. After refrigeration, 89 mg. of O-acetyltetrahydroerysodine, m. p. 135–136°, was obtained.

Anal. Calcd. for $C_{20}H_{27}NO_4$: C, 69.54; H, 7.87; CH_3CO-, 12.46. Found: C, 69.43, 69.63; H, 7.86, 7.91; CH_3CO-, 12.21.

Tetrahydroerysopine Hydrobromide.—One gram of erysopine was dissolved in a mixture of 25 ml. of water and 1.5 ml. of 40% aqueous hydrobromic acid. After the addition of 124 mg. of Adams platinum catalyst, the hydrogenation was carried out at atmospheric pressure, and 2 moles of hydrogen was absorbed. After removal of the catalyst, the filtrate was concentrated to dryness at 30° under reduced pressure in an atmosphere of nitrogen. The colorless gum was dissolved in 5 ml. of hot absolute ethanol and crystals quickly formed in the hot solution. The solution was cooled in the refrigerator. After the crystallization was complete, the yield of tetrahydroerysopine hydrobromide was 1.024 g.; m. p. 242–244°. Two recrystallizations of this product from ethanol yielded 900 mg. of tetrahydroerysopine hydrobromide which melted constantly at 244–245°.

Anal. Calcd. for $C_{17}H_{23}NO_3 \cdot HBr$: C, 55.15; H, 6.53. Found: C, 55.19; H, 6.50.

Tetrahydro-"erysocine" Hydrobromide.—A sample of "erysocine" was hydrogenated under conditions similar to that described for erysopine. The first crop of tetrahydro-"erysocine" hydrobromide melted at 223–224°. After recrystallization from absolute ethanol and ether, the melting point of the product was unchanged.

Anal. Calcd. for $C_{18}H_{25}NO_3 \cdot HBr$: C, 56.25; H, 6.91. Found: C, 56.11; H, 6.64.

It was interesting that this product showed no ready tendency to separate into tetrahydroerysodine hydrobromide and tetrahydroerysovine hydrobromide.

Erysovine Hydrobromide Hemi-hydrate.—To 5 ml. of absolute alcohol containing 300 mg. of erysovine was added 80 mg. of anhydrous gaseous hydrogen bromide in 2 ml. of alcohol. This solution was diluted with 4 ml. of anhydrous ethyl ether and refrigerated. Crystals separated slowly during three days; they weighed 197 mg. and melted at 150–151° (dec.). One recrystallization of this product did not alter the melting point.

Anal. Calcd for $C_{18}H_{21}NO_3 \cdot HBr \cdot 0.5H_2O$: C, 55.54; H, 5.95; N, 3.59. Found: C, 55.48; H, 6.06; N, 3.68.

Erysovine Hydriodide Hydrate.—A 300-mg. sample of erysovine was dissolved in 5 ml. of absolute ethanol and 150 mg. of sodium iodide was added. The solution was acidified with two drops of glacial acetic acid, diluted with 3 ml. of ethyl ether, and refrigerated. After one week, 121 mg. of crystals melting at 159–160° was obtained. Recrystallization of this product from ethanol and ether yielded 63 mg. of hydriodide melting at 162°.

Anal. Calcd. for $C_{18}H_{21}NO_3 \cdot HI \cdot H_2O$: C, 48.54; H, 5.43; N, 3.14. Found: C, 48.76; H, 5.52; N, 3.22.

Conversion of Erysodine into Erysotrine Methomethylsulfate.—A mixture of 20 ml. of 5% sodium hydroxide solution, 150 mg. of erysodine, and 1 ml. of dimethyl sulfate was shaken for five minutes at 25°. The excess dimethyl sulfate was hydrolyzed by warming the solution and the cooled clear alkaline solution was extracted four times with chloroform. Distillation of the solvent left 143 mg. of a clear gum which was dissolved in 1 ml. of absolute ethanol. The crystals, which formed during refrigeration, melted at 60°. The melting point was constant at 61° after two recrystallizations of the product from ethanol. The crystals were somewhat hygroscopic.

Anal. Calcd. for $C_{21}H_{29}NO_7S$: C, 57.39; H, 6.65; N, 3.16. Found: C, 57.46, 57.47; H, 6.96, 6.90; N, 3.15.

Conversion of Erysopine into Erysotrine Methomethylsulfate.—A 1.087-g. sample of erysopine was dissolved in 50 ml. of 10% sodium hydroxide solution and 2 ml. of dimethyl sulfate was added. After shaking the mixture vigorously for twenty-five minutes with cooling, the excess dimethyl sulfate was hydrolyzed by heating the solution to 50°. After cooling, the alkaline solution was extracted five times with chloroform. Distillation of the solvent left 1.313 g. of residue which crystallized when it was dissolved in 2 ml. of absolute ethanol. The crystals melted at 60–61° and when mixed with the substance de-

rived from erysodine, the melting point of the mixture was not depressed. A sample was dried four hours at 25° *in vacuo* for analyses.

Anal. Calcd. for $C_{21}H_{29}NO_7S$: C, 57.39; H, 6.65. Found: C, 57.75; H, 6.43.

Conversion of Erysodine N-Oxide to Erysodine.—A 470-mg. sample of erysodine was added to 5 ml. of superoxol and the mixture was heated forty-five minutes on the steam-bath. After standing overnight, the solution was concentrated *in vacuo*. The residue, 596 mg., was dissolved in 10 ml. of 15% hydrochloric acid. Two grams of zinc dust was added in small portions and after the reaction had subsided the solution was filtered. The filtrate was made alkaline with ammonium hydroxide and extracted five times with 10-ml. portions of chloroform. Distillation of the chloroform left 143 mg. (30%) of product, m. p. 189°. One recrystallization of this product from ether gave erysodine, m. p. 200–202°. A mixture of this product and the original erysodine showed no depression of melting point.

Conversion of Erysodine into Erysotrine and Erysotrine Picrate.—A 2-g. sample of erysodine was added to 20 ml. of superoxol (30% hydrogen peroxide), and the solution was heated for one hour on the steam-bath. Concentration of the solution at 18 mm. pressure yielded 3.093 g. of a thick oil. This crude N-oxide was dissolved in 50 ml. of 2% sodium hydroxide solution, and 5 ml. of dimethyl sulfate was added. The mixture was shaken for one hour, with occasional addition of alkali to keep the solution alkaline. The solution was extracted six times with chloroform, and distillation of the solvent *in vacuo* left 1.308 g. of crude erysotrine N-oxide. This product was dissolved in 50 ml. of 15% hydrochloric acid solution and reduced by gradual addition of 5 g. of zinc dust. After hydrogen evolution had practically ceased, the zinc sludge was collected on a filter and the filtrate was made alkaline with ammonium hydroxide. The solution was extracted six times with chloroform, and distillation of the solvent *in vacuo* left 963 mg. of crude erysotrine as a gum. This product did not crystallize from ether, so a 599-mg. portion was dissolved in 5 ml. of absolute ethanol and 500 mg. of picric acid was added. After standing, the clear yellow solution deposited crystals; m. p. 157°. Five recrystallizations from ethanol yielded pure erysotrine picrate, which melted constantly at 160–161°; $[\alpha]^{25}D$ + 138.1° (*c*, 0.35 in ethanol).

Anal. Calcd. for $C_{19}H_{23}NO_3 \cdot C_6H_3N_3O_7$: C, 55.39; H, 4.83; 3 CH_3O-, 17.17. Found: C, 55.48; H, 4.70; CH_3O-, 16.42.

The gummy erysotrine was sublimed in a molecular still at a bath temperature of 100–105° and a pressure of 2.5×10^{-4} mm. The sublimate was gummy and showed no tendency to crystallize.

Anal. Calcd. for $C_{19}H_{23}NO_3$: C, 72.81; H, 7.39, 3 CH_3O-, 29.74. Found: C, 72.46; H, 7.64.

Resublimation gave a product of unaltered composition. Found: C, 72.46; H, 7.35; CH_3O-, 26.45.

Conversion of Erysovine into Erysotrine Picrate.—To 20 ml. of superoxol was added 276 mg. of erysovine and the solution was warmed to 90°. It was then cooled and maintained at 10° for six hours. After concentration *in vacuo*, 285 mg. of crude erysovine N-oxide remained. It was dissolved in 25 ml. of 4% sodium hydroxide solution and 5 ml. of dimethyl sulfate was added. The mixture was mechanically agitated for one hour; alkali was added to maintain an alkaline reaction. The solution was then extracted with chloroform ten times and distillation of the solvent left 270 mg. of crude erysotrine N-oxide. It was dissolved in 25 ml. of dilute hydrochloric acid and reduced by the gradual addition of 5 g. of zinc dust. When the reduction was complete, the zinc sludge was removed and the filtrate was made alkaline with ammonium hydroxide and extracted ten times with chloroform. Removal of the solvent *in vacuo* yielded 169 mg. of crude erysotrine. It was dissolved in 5 ml. of warm ethanol and treated with 5 ml. of warm ethanol containing 129 mg. of picric acid. The solution was maintained at 50–60° for six hours for crystallization. Filtration yielded 122 mg. of yellow crystals; m. p., 158–160°, $[\alpha]^{25}D$ + 137°. Recrystallization of this product yielded 65 mg. of erysotrine picrate, m. p. 160–161°. The melting point of a mixture of this picrate and the corresponding picrate derived from erysodine was not depressed. The rotation, $[\alpha]^{25}D$ + 139°, checked that of erysotrine picrate from erysodine.

Conversion of Erysopine into Erysotrine Picrate.—A 272-mg. sample of erysopine was added to 20 ml. of superoxol and the mixture was heated at 100° for thirty minutes. The insoluble alkaloid was filtered (32 mg.) and discarded. Concentration of the filtrate *in vacuo* left 282 mg. of crude erysopine N-oxide. It was dissolved in 50 ml. of 4% sodium hydroxide solution and after adding 5 ml. of dimethyl sulfate, the mixture was shaken one hour. After extraction eight times with chloroform, the combined extracts were concentrated *in vacuo;* 30.7 mg. of erysotrine N-oxide remained. Eight more extractions yielded only 6.5 mg. of oxide. The combined product was dissolved in 25 ml. of dilute hydrochloric acid, and reduced with 3 g. of zinc dust. The filtrate from the residual zinc was made ammoniacal and extracted eight times with chloroform. Distillation of the solvent *in vacuo* left 14 mg. of crude erysotrine, and further extractions yielded 4 mg. The 18 mg. of erysotrine was dissolved in 1 ml. of ethanol and treated with 15 mg. of picric acid dissolved in 1 ml. of ethanol. After addition of 2 drops of petroleum ether, crystals formed slowly and crystallization was allowed to continue overnight at 10°. The yield of crystals was 14 mg. and two recrystallizations from ethanol and petroleum ether gave 7 mg. of pure erysotrine picrate, m. p. 160–161°, $[\alpha]^{25}D$ + 138°. A mixture of this picrate and the one derived similarly from erysodine did not show a depressed melting point.

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Summary

Erysodine, erysovine and erysopine have the same four-nuclei ring system; each has three oxygen atoms at the same positions on the ring system, but each differs in the position or number of O-methyl groups. These deductions are based essentially upon the results of analytical, hydrogenation and methylation experiments.

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