0.2 g. (5 millimoles) of lithium aluminum hydride. The solution was refluxed 12 hours, and produced a crude solid which was crystallized twice from ethanol to give 0.6 g., 88%, of needles or plates, m.p. 87°. Two forms were observable, plates and somewhat opaque needles. The former sintered slightly below 87° but resolidified and remelted at 87°, $[\alpha]^{26}D$ −34°.

Anal. Calcd. for $C_{28}H_{48}$: C, 87.42; H, 12.58. Found: C, 87.64; H, 12.42.

3-β-Methylcholestane (IX).—Hydrogenation at one atm. of 0.20 g. of the methylcholestene in 80 ml. of acetic acid over 60 mg. of 10% palladium on charcoal at 80° required two hours. After filtering hot and reducing the volume of solvent to 20 ml. and cooling, 0.170 g. of crystals m.p. 97–98° separated. A second crop 0.02 g. was obtained, yield 95%. Crystallization from ethanol, 12 ml., did not change the m.p., lit.[8] 96–97°. Two crystalline forms were again observed. About 5° below the m.p. the plates changed to a needle form $[\alpha]^{25}D$ +11°.

Anal. Calcd. for $C_{28}H_{50}$: C, 86.97; H, 13.03. Found: C, 87.43; H, 12.94.

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The Identification of Sagittol as Eudesmol

BY PETE D. GARDNER AND W. J. HORTON

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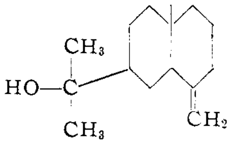
Twenty-five years ago, Yanovsky[1] reported the isolation of a $C_{15}H_{26}O$ alcohol from the steam-distillable portion of the root-cortex of *Balsamorrhiza sagittata* (Pursh) Nutt to which he assigned the name sagittol. His evidence for the hydroxyl function consisted of the formation of an acetate derivative upon refluxing the alcohol with sodium acetate in acetic anhydride.

The structure determination of this nature product was undertaken in these laboratories and a parallel of the chemistry of it with that of eudesmol[2] (I) soon became apparent. Hydrogenation to a dihydro derivative (m.p. 85–86°) and dehydrogenation with palladium–charcoal to eudaline (identified as the picrate) indicated it to be a bicyclic unsaturated alcohol. The similarity of physical constants of these compounds with those in the eudesmol series prompted a comparison with authentic material[3] which established the identity of dihydrosagittol as dihydroeudesmol. The acetate of sagittol was prepared and although its purification was somewhat troublesome its properties corresponded satisfactorily with those reported for both sagittol acetate[1] and eudesmol acetate.[1,2] The specific rotation of sagittol previously reported[1] differed significantly from the value found in the present study and rigorous purification of a sample made the comparison even less satisfactory. Several crystallizations from different solvents did not appreciably alter the melting point although subsequent fractional sublimation of a sample proved the presence of a small amount of a more volatile oily contaminant. The melting point of material thus prepared was not changed but the specific rotation was altered. This second fraction, although too small to permit an investigation, was more negative in specific rotation than sagittol.



I

The suggestion has been made[4] that sagittol may be identical with cryptomeridol.[5] This is necessarily so in light of the identity established here and that established between cryptomeridol and machilol[6] and between machilol and eudesmol.[7] Thus, it would appear that *Balsamorrhiza sagittata* is another of the many sources of eudesmol. Difficulty in the purification of eudesmol is evidenced by the variance in specific rotations reported on material isolated from its various sources (see Experimental section).

One striking dissimilarity with previous work noted in this study was the product resulting from an attempted dehydration of sagittol to the diolefin (eudesmene) using formic acid. Analytical data indicated it to be the formate ester.

Experimental

Isolation of Sagittol.—Sixty pounds of the damp root-cortex[8] was broken into small pieces and steam-distilled in four batches. The first organic material obtained consisted of a light oil which was followed immediately by crude saggitol as a cotton-like solid. The distillation of each batch was discontinued after a total of 20 l. of water had been collected. Material so obtained (70 g., m.p. 75–78°) was purified by one crystallization from petroleum ether (30–40°) to give 51 g. of colorless solid, m.p. 79–80°. Two additional crystallizations from methanol and water and two from petroleum ether did not change the melting point. Fractional sublimation of this material at 40° (0.3 mm.) afforded a very small amount of light oil mixed with some solid, $[\alpha]^{20}D$ +5.2°. Later fractions were beautifully crystalline, m.p. 79–80°, $[\alpha]^{20}D$ +37.2° (2.31% in ethanol). Constants previously reported for this substance: sagittol,[1] m.p. 77–78°, $[\alpha]^{20}D$ +25.8°; machilol,[9] m.p. 79–80°, $[\alpha]^{25}D$ +30.08°; cryptomeridol,[4,6] m.p. 84°, 79–80°, $[\alpha]^{19}D$ +19.78°, +24.2°; eudesmol,[7] m.p. 82–83°, $[\alpha]D$ +31°.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02, H, 11.79. Found: C, 80.91; H, 11.84.

Conversion to Eudaline.—A 2.0-g. sample of purified sagittol was heated at 300° with 1.0 g. of palladium–charcoal[10] for 4 hr. in a nitrogen atmosphere. Isolation in the usual manner followed by treatment of the resulting liquid with picric acid gave 0.91 g. of eudaline picrate, m.p. 92–93° (lit.[11] 90–91°).

Dihydrosagittol.—Some difficulty was encountered in the reduction in that it was too slow to be practical in ethanol or methanol and was accompanied by hydrogenolysis in acetic acid as a solvent. The following represents the most satisfactory conditions found.

A 5.0-g. sample of highly purified sagittol dissolved in 35 ml. of methanol and 5 ml. of acetic acid was shaken at room temperature with 0.10 g. of platinum oxide under one at-

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(1) E. Yanovsky, THIS JOURNAL, **52**, 3446 (1930).

(2) L. Ruzicka, A. H. Wind and D. R. Koolhaas, *Helv. Chim. Acta*, **14**, 1132 (1931).

(3) We are indebted to Professor O. Jeger who kindly provided an authentic sample of dihydroeudesmol, m.p. 81–83°.

(4) J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, London, 1952, p. 192.

(5) H. Wienhaus and H. Scholz, *Ber. Schimmel & Co., Akt.-Ges.*, 269 (1929); *C. A.*, **24**, 1933 (1930).

(6) Y. Sugii and T. Sengoku, *J. Pharm. Soc. Japan*, **51**, 196 (1931); *C. A.*, **25**, 2989 (1931).

(7) L. Ruzicka, D. R. Koolhaas and A. H. Wind, *Helv. Chim. Acta*, **14**, 1178 (1931).

(8) Plants were collected in Salt Lake Valley, Utah, in June, 1954.

(9) S. Takagi, *J. Pharm. Soc. Japan*, **473**, 565 (1921); *C. A.*, **16**, 1578 (1922).

(10) N. D. Zelinsky and M. B. Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

(11) L. Ruzicka, J. Meyer and M. Mingazzini, *Helv. Chim. Acta*, **5**, 345 (1922).

mosphere of hydrogen. The theoretical volume of hydrogen was absorbed in 90 min. and the product (4.9 g.) was obtained in the usual manner, m.p. 81–85°. Two crystallizations from methanol and water afforded (in two crops) 3.9 g. of colorless crystals, m.p. 85–86°. The sample for analysis was obtained by sublimation at 80° (0.1 mm.) and had the same m.p., $[\alpha]^{19}\text{D}$ +23.1° (1.38% in ethanol) (lit.[2] $[\alpha]\text{D}$ +17°). The m.p. of a sample mixed with dihydroeudesmol[3] was unchanged.

Anal. Calcd. for $C_{15}H_{26}O$: C, 80.24; H, 12.58. Found: C, 80.33; H, 12.42.

Sagittol Acetate.—A mixture consisting of 10.0 g. of sagittol, 25 ml. of acetic anhydride and 1.0 g. of freshly fused sodium acetate was refluxed for 45 min. and then stirred with water (200 ml.) for 3 hr. Extraction with ether followed by distillation afforded 10.5 g. of the ester, b.p. 105–115° (0.75 mm.), which was contaminated with starting material. The only satisfactory means of purification consisted of passing this material in 50 ml. of petroleum ether (30–50°) through a column of acid-washed alumina (30 g.). After washing the column with 300 ml. of 10% ether in petroleum ether (30–50°) the combined solutions were freed from solvent by distillation through a 30-cm. bead-packed column. Upon further distillation through a 10-in. Vigreux column there was obtained 7.5 g. of sagittol acetate, b.p. 107.5–109.5° (0.75 mm.), $n^{20}\text{D}$ 1.4915, $[\alpha]^{19}\text{D}$ +30.2° (1.15% in ethanol). This compound is reported[12] to have $n^{20}\text{D}$ 1.49204 and $[\alpha]^{20}\text{D}$ +31°.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.22; H, 11.18. Found: C, 77.45; H, 11.21.

Treatment of Sagittol with Formic Acid.—Six grams of sagittol was refluxed for 45 min. with 30 ml. of 90% formic acid. Extraction with ether and isolation in the usual manner afforded 5.3 g. of colorless liquid, b.p. 77–78° (1.0 mm.), $n^{20}\text{D}$ 1.5149, $[\alpha]^{19}\text{D}$ −7.14° (1.18% in ethanol).

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.97; H, 10.41.

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[12] F. W. Semmler and E. Tobias, *Ber.*, **46**, 2026 (1913).

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The Synthesis of Nitrogen-containing Ketones. III. Studies with 2-Methyl-5-ethylpyridine, 2,4-Lutidine and Lepidine[1]

BY NEWTON N. GOLDBERG AND ROBERT LEVINE

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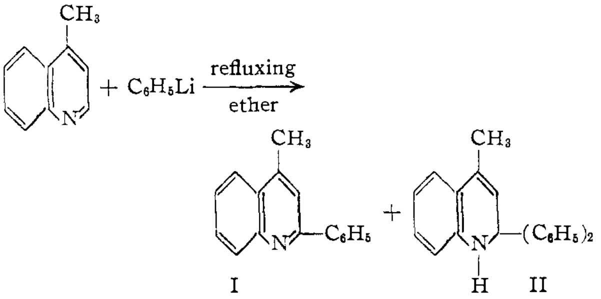
Earlier papers from this Laboratory[2,3] have been concerned with the acylation of 2-picoline, quinaldine and 2,6-lutidine. The present report is an extension of our work to other tar bases.

Reaction of two equivalents of the lithium derivative of 2,4-lutidine or 2-methyl-5-ethylpyridine with one equivalent of methyl benzoate as described earlier[2,3] gave 2-phenacyl-4-methylpyridine (89%) and 2-phenacyl-5-ethylpyridine (83%), respectively. Both of these ketones gave copper salts when treated with copper(II) acetate solution and may have some application as chelating agents.

The acylation of lepidine has been studied by other investigators.[4,5] Although Bergstrom and Moffat[4] reported that they were unable to acylate lepidine with ethyl benzoate using sodium amide as the condensing agent, a reinvestigation of this reaction by Weiss and Hauser[5] has shown that the benzoylation and other acylations of lepidine may be effected in low yields in the presence of sodium amide.

We have attempted to metalate the methyl group of lepidine by treating it with phenyllithium in refluxing ether. However, metalation did not take place since the reaction of the mixture with esters, acid halides or carbon dioxide did not result in acylation or carboxylation of the methyl group. In all cases a mixture of 2-phenyl-4-methylquinoline (I) (61–66%) and 2,2-diphenyl-4-methyl-1,2-dihydroquinoline (II) (24–26%) was obtained.



I II

These results show the importance of temperature on the course of the reaction since Tarbell and co-workers[6] have shown that when this reaction is effected at ice-bath temperature only I (54%) is obtained.

The structure of II was established by oxidizing it with potassium ferricyanide[7,8] to give the corresponding carboxylic acid which was then decarboxylated by calcium oxide[9] to give the known 2,2-diphenyl-1,2-dihydroquinoline.[10]

Experimental[11]

The Benzoylation of 2,4-Lutidine and 2-Methyl-5-ethylpyridine.—Using the method described earlier for similar reactions,[2,3] the interaction of phenyllithium (0.2 mole) and methyl benzoate (13.6 g., 0.1 mole) gave 18.8 g. (89%) of 2-phenacyl-4-methylpyridine, b.p. 159–160° at 1.8 mm. *Anal.* Calcd. for $C_{14}H_{13}NO$: C, 75.59; H, 6.20; N, 6.68. Found: C, 79.58; H, 6.11; N, 6.83. The ketone gave a yellow picrate, m.p. 167–168° (from 95% ethanol). *Anal.* Calcd. for $C_{20}H_{16}N_4O_8$: N, 12.72. Found: N, 12.91. The ketone also gave a tan copper salt, m.p. 171–172° dec. *Anal.* Calcd. for $C_{28}H_{24}N_2O_2Cu$: N, 5.79. Found: N, 5.54.

From a similar sized run involving 2-methyl-5-ethylpyridine there was obtained 18.7 g. (83% of 2-phenacyl-5-ethylpyridine, b.p. 169–171° at 1.8 mm., m.p. 64–65° (from 60–70° petroleum ether). *Anal.* Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.99; H, 6.95; N, 5.97. The ketone gave a yellow picrate, m.p. 163.8–164.2° (from 95% ethanol). *Anal.* Calcd. for $C_{21}H_{18}N_4O_8$: N, 12.33. Found: N, 12.12. The ketone also gave a brown copper salt, m.p. 168–169° dec. *Anal.* Calcd. for $C_{30}N_{28}N_2O_2Cu$: N, 5.47. Found: N, 5.26.

Reaction of Lepidine with Phenyllithium.—An ether solution of phenyllithium (0.4 mole) and lepidine (0.4 mole) was refluxed for 30 minutes and then poured onto 150 ml.

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[1] This work was performed under Contract No. AT(30-1)-670 between the U. S. Atomic Energy Commission and the University of Pittsburgh.

[2] N. N. Goldberg, L. B. Barkley and R. Levine, This Journal, **73**, 4301 (1951).

[3] N. N. Goldberg and R. Levine, *ibid.*, **74**, 5217 (1952).

[4] F. W. Bergstrom and A. Moffat, *ibid.*, **59**, 1494 (1937).

[5] M. J. Weiss and C. R. Hauser, *ibid.*, **71**, 2023 (1949).

[6] D. S. Tarbell, J. F. Bunnett, R. B. Carlin and V. P. Wystrach, *ibid.*, **67**, 1584 (1945).

[7] L, Ruzicka, G. B. R. de Graaff and J. R. Hosking, *Helv. Chim. Acta*, **9**, 976 (1926); **14**, 238 (1931).

[8] R. Weissgerber and O. Kruber, *Ber.*, **52**, 352 (1919).

[9] W. Koenigs, *ibid.*, **12**, 98 (1879).

[10] H. Gilman and G. C. Gainer, This Journal, **69**, 877 (1947).

[11] The tar bases for this study were supplied through the courtesy of Dr. F. E. Cislak, Reilly Tar and Chemical Corp.