H, 6.9; OCH_3, 30.1. Found: C, 46.7; H, 6.85; OCH_3, 30.0.)

The dimethyl-mannonolactone gave a phenylhydrazide $[\alpha]^{18}D$ −25° in water (*c*, 0.5), m. p. 158° (from methyl alcohol–ether) which crystallized upon cooling and then remelted at 168°. (*Anal.* Calcd. for $C_{14}H_{22}O_6N_2$: N, 8.9; OCH_3, 19.7. Found: N, 8.8; OCH_3, 20.0.) The phenylhydrazide prepared from 5 mg. of the lactone of Goodyear and Haworth[19] had m. p. 158°, the melt crystallizing and remelting at 168–169°. It gave no depression of the m. p. when in admixture with the phenylhydrazide of 2,3-dimethyl-D-mannonic acid obtained above. The 2,3-dimethyl-D-mannono-γ-lactone could be regenerated from its phenylhydrazide by the usual procedure.

Examination of the glycosides derived from methylated carob gum in two other experiments confirmed the above results and enabled the material, corresponding to Fraction V, to be identified as mainly methyl-2,3-dimethyl-D-mannoside. The intermediate fractions which distilled between methyl-2,3,4,6-tetramethyl-D-galactoside and methyl-2,3,6-trimethyl-D-mannoside were shown to be composed only of these two substances.

Preparation of 2,3,6-Trimethyl-D-mannose and its Derivatives.—Crude ivory-nut mannan was methylated with methyl sulfate and sodium hydroxide. A sample of methylated mannan (10 g.) which, after four methylations, had $[\alpha]^{18}D$ −52° in water (*c*, 0.7); OCH_3, 44.2,[17] was subjected to methanolysis with 3% methyl alcoholic hydrogen chloride. The mixture of glycosides (10.84 g.) was subjected to fractional distillation. A portion of the methyl-2,3,6-trimethyl-D-mannoside (4.31 g., $n^{15}D$ 1.4620) thus produced was transformed into 2,3,6-trimethyl-mannose $[\alpha]^{15}D$ −5.5° in water (*c*, 2.0), OCH_3, 41.3. From this trimethyl sugar there were isolated by the methods already given above: (a) 2,3,6-trimethyl-D-mannose anilide, m. p. 129° (after crystallization from ethyl alcohol), $[\alpha]^{15}D$ −150° in methyl alcohol (*c*, 0.5) changing to −38°. (Found: C, 60.65; H, 7.85; N, 4.6; OCH_3, 30.8.) (b) 2,3,6-Trimethyl-D-mannono-γ-lactone, m. p. 83–84° (after recrystallization from ethyl acetate–ether), $[\alpha]^{15}D$ +69° initial value in water (*c*, 1.5) changing in one hundred and fifty days to +38° (constant value). The acid, obtained by addition of dilute sulfuric acid to a solution of the sodium salt formed by warming the lactone with dilute sodium hydroxide, showed $[\alpha]^{18}D$ −18.5 changing in twenty-three days to +40°. (Found: C, 49.25; H, 7.3; OCH_3, 42.3.) (c) The amide of 2,3,6-trimethyl-D-mannonic acid, m. p. 125° (after crystallization from dioxane). (*Anal.* Calcd. for $C_9H_{19}O_6N$: OCH_3, 39.2. Found: OCH_3, 39.8.) (d) The phenylhydrazide of 2,3,6-trimethyl-D-mannonic acid, m. p. 131°, $[\alpha]^{18}D$ −18° in water (*c*, 1.7) (after crystallization from ethyl alcohol–ether). (Found: N, 8.4; OCH_3, 28.3.)

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Summary

Carob gum, a polysaccharide, obtained from the seeds of the carob bean, is composed of D-galactose (20%) and D-mannose (80%). The methylated gum, obtained either directly or through the acetate by the agency of methyl sulfate and sodium hydroxide, gives upon methanolysis the glycoside of 2,3,4,6-tetramethyl-D-galactose (1 part,) 2,3,6-trimethyl-D-mannose (2–3 parts) and 2,3-dimethyl-D-mannose (1 part). These constituents have been identified by the formation of crystalline derivatives. The structure of the galactomannan polysaccharide is discussed.

ST. PAUL, MINN
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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL]

The Papilionaceous Alkaloids. IV. *Baptisia perfoliata* (L.) R. Br.[1]

BY LÉO MARION AND FRANÇOIS TURCOTTE

Until recently the genus *Baptisia* has been in a confused state,[2] but *B. perfoliata* (L.) R. Br. is one of the well-established species and no doubt seems to have existed concerning its identity. However, no study of its alkaloid content had ever been made and the results of such an investigation are now reported. The plant contains at least six alkaloids, four of which, *i. e.*, *d*-sparteine, cytisine, N-methylcytisine and anagyrine are known, while the fifth, isolated in very small quantity, only, seems to be identical with alkaloid P_2, previously reported as occurring in *B. australis*.[3] The sixth, alkaloid P3, appears to be new and it is proposed to designate it as baptifoline; it is crystalline and forms easily crystallizable salts. Until further characterized it is best represented by $C_{15}H_{20}O_2N_2$.

Experimental

The plant used in this investigation was grown at the Dominion Experimental Farm, Ottawa, through the courtesy of Dr. H. A. Senn, whom we wish to thank. The dried and ground material (wt. 4285 g.) was extracted in soxhlets with methanol and the extract evaporated until the solvent was largely removed. The residue was diluted with water, made acid to congo red by the addition of hydrochloric acid and heated on the steam-bath for eight hours. The mixture was cooled, filtered with suction and the insoluble matter again heated with dilute hydrochloric acid, cooled and filtered. The combined filtrate was extracted repeatedly with ether (extract A). During this extraction a crystalline solid separated which was filtered and washed with water. The combined filtrate and washings was alkalized with ammonia and extracted with chloroform in a continuous liquid-liquid extractor (extract B).

Isolation of a Neutral Substance.—The solid substance that had separated was also obtained from ether extract (A) from which it crystallized on standing. After several recrystallizations from boiling methanol in which it is only sparingly soluble, the colorless, neutral substance

(1) Published as National Research Council Bull. No. 1731.
(2) Mary M. Larisey, *Ann. Missouri Botan. Gard.*, **27**, 119 (1940).
(3) L. Marion and J. Ouellet, THIS JOURNAL, **70**, 691 (1948).

consisted of small, colorless, prismatic needles, m. p. 218°.[4] This crystalline substance dissolves in aqueous sodium hydroxide giving a yellowish brown solution from which it is not precipitated by acids.

Anal. Found: C, 69.07, 69.04; H, 4.58, 4.56. Calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.13.

The chloroform extract (B) was evaporated to dryness, the residual bases warmed with dilute hydrochloric acid and the cooled solution filtered through charcoal. The acid filtrate was extracted repeatedly with ether, alkalized with ammonia and extracted with chloroform in a continuous liquid–liquid extractor. The chloroform extract, on evaporation to dryness, yielded the crude bases as a soft brown gum, wt. 8.0 g. The crude alkaloid was first fractionated *in vacuo* into a distillate boiling up to 210° (0.2 mm.) and a residue R. The distillate was again distilled *in vacuo* and the following fractions collected; I, b. p. 100–125° (0.2 mm.), a colorless oil, wt. 0.949 g.: II, b. p. 135–150° (0.2 mm.), a colorless oil which partly crystallized on cooling, wt. 0.818 g.; III, b. p. 150–165° (0.2 mm.), a thick oil which crystallized on cooling, wt. 0.3 g.; IV, b. p. 165–180° (0.2 mm.), a mixture of crystals and yellow oil, wt. 0.856 g.; V, b. p. 180–200° (0.2 mm.), a viscous, yellow oil, wt. 0.141 g.; and an undistilled residue.

Isolation of *d*-Sparteine.—The base obtained as fraction I was dissolved in methanol and the solution divided into two equal portions. The first portion was added to a hot methanolic solution of picric acid. A picrate separated which, after recrystallization from boiling methanol, consisted of silky, yellow needles, m. p. 208° either alone or after admixture with an authentic sample of *d*-sparteine dipicrate (m. p. 208°). The second portion of the methanolic solution of the base was made just acid to congo red by the cautious addition of 65% perchloric acid. Water was then added and the solution heated on the steam-bath until the methanol had evaporated. The addition of a few drops of ammonia to the cooled solution caused the separation of a crystalline perchlorate which after one crystallization from methanol–ether melted at 173° either alone or after admixture with an authentic sample of *d*-sparteine perchlorate.

A quantity of the base, liberated from the recrystallized picrate, was distilled *in vacuo*, b. p. 110° (0.2 mm.); it has $[\alpha]^{22}D$ +15.8 (*c*, 1.21 in absolute ethanol).

Isolation of Cytisine.—The partially crystallized distillate obtained as fraction II was dissolved in boiling ether. The solution, on standing, deposited a crystalline base which after a further crystallization from ether, separated as colorless needles, melting at 154.5° and in admixture with cytisine at 155°.

Anal. Calcd. for $C_{11}H_{14}ON_2$: N, 14.75. Found: N, 14.67, 14.72.

A small quantity of the base was converted by the usual method to the perchlorate which separated from methanol as colorless needles melting at 286° and, in admixture with an authentic sample of cytisine perchlorate, at 287–288°. A further small quantity of the base was converted to the picrate by addition of its solution in methanol to methanolic picric acid. Recrystallized from water or from acetone–methanol, it melts at 286° and, when mixed with cytisine picrate, at 287°. Fraction III also yielded cytisine.

Isolation of N-Methylcytisine.—The ether mother liquor of fraction II from which cytisine had crystallized was evaporated to dryness and the residual base converted to picrate. Recrystallization of this picrate from water yielded a further quantity of cytisine picrate. Concentration of the aqueous mother liquor caused the separation of another picrate which, after recrystallization from methanol, was obtained as long, lemon-yellow needles melting at 233°, either alone or after admixture with N-methylcytisine picrate.

(4) All melting points are corrected.

Anal. Calcd. for $C_{12}H_{16}ON_2 \cdot C_6H_3O_7N_3$: N, 16.16. Found: N, 16.02, 16.19.

Isolation of Anagyrine.—The viscous, resinous oil obtained as fraction V was dissolved in methanol and the solution made just acid to congo red by the cautious addition of 65% perchloric acid. The crystalline perchlorate thus obtained was recrystallized several times from boiling methanol from which it separated as colorless needles melting at 315°, either alone or in admixture with anagyrine perchlorate.[5] The perchlorate was dissolved in water, the solution alkalized with ammonia and extracted with chloroform. The base obtained by evaporation of the chloroform solution was dissolved in methanol and added to a methanolic solution of picric acid. A picrate separated as yellow needles, m. p. 252° and the melting point was unaltered by admixture with anagyrine picrate.

Anal. Calcd. for $C_{15}H_{20}ON_2 \cdot C_6H_3O_7N_3$: C, 53.27; H, 4.86. Found: C, 53.59, 53.69; H, 4.70, 4.82.

Fraction IV yielded both cytisine and anagyrine.

Isolation of Baptifoline (Alkaloid P3).—The undistilled residue from the bases was subjected to distillation at 10^{-4} mm. At 180–210°, there was obtained a fraction which was dissolved in methanol and the solution made just acid to congo red with 66% perchloric acid. A perchlorate separated which after several recrystallizations from boiling methanol consisted of colorless plates, m. p. 286–287°. The perchlorate was dissolved in water, the solution alkalized with ammonia and extracted with chloroform. The base recovered from the extract crystallizes from acetone–ether as colorless plates, m. p. 210°. When mixed with thermopsine (m. p. 210°) the mixture was all liquid at 192°.

Anal. Calcd. for $C_{15}H_{20}O_2N_2$: C, 69.18; H, 7.74; N, 10.76. Found: C, 68.55; H, 7.29; N, 10.60.

The base forms a picrate that crystallizes from methanol as yellow needles; it sinters at 145° and melts at 256°.

Anal. Calcd. for $C_{15}H_{20}O_2N_2 \cdot C_6H_3O_7N_3 \cdot CH_3OH$: C, 50.66; H, 5.22; N, 13.44. Found: C, 50.82, 50.82; H, 4.98, 5.04; N, 12.38, 12.54.

Isolation of Alkaloid P2.—On concentration, the mother liquor from the crystallization of baptifoline perchlorate yielded a further quantity of the same base perchlorate which was filtered. The filtrate was diluted with water, heated on the steam-bath until the organic solvent was evaporated and alkalized with ammonia. The liberated base was extracted with chloroform, the extract evaporated on the steam-bath and the basic residue, dissolved in methanol, was added to a methanolic solution of picric acid. On standing, this solution deposited a very small quantity of a picrate which, after recrystallization from acetone–methanol, sintered slightly at 185° and melted at 241°. The melting point was unaltered by admixture with the picrate of alkaloid P2, previously isolated from *Baptisia australis*.[5] Insufficient material was obtained for a complete analysis.

Anal. Found: C, 50.36, 50.18; H, 5.11, 5.03.

Summary

1. *Baptisia perfoliata* (L.) R. Br., has been found to contain at least six alkaloids, four of which, *i. e.*, *d*-sparteine, cytisine, N-methylcytisine and anagyrine are known.

2. The fifth alkaloid, present as a trace, appears identical with alkaloid P2, also present in small quantity in *B. australis*.

3. Baptifoline, the remaining base, seems to be new.

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(5) L. Marion and J. Ouellet, THIS JOURNAL, 70, 3076 (1948).