THE RESOLUTION OF SPARTEINE

Sir:

In consideration of the recently reported syntheses of sparteine[1,2] we wish to record herein the resolution of *dl*-sparteine, the total synthesis of which was first announced from this Laboratory.[3] Synthetic *dl*-sparteine was resolved by means of β-camphorsulfonic acid, and both *d*- and *l*-sparteine were isolated and identified.

Equimolar portions of racemic sparteine and *d*-β-camphorsulfonic acid in ethanol gave ***l*-sparteine *d*-β-camphorsulfonate.** After two recrystallizations from acetone the specific rotation remained constant, $[\alpha]^{29}\text{D}$ 24.8 ± 0.5° (*C*, 1.932 in chloroform), and consistent with that of an authentic sample of the *d*-β-camphorsulfonate of natural *l*-sparteine, $[\alpha]^{29}\text{D}$ 24.4 ± 0.5° (*C*, 2.298 in chloroform). Both natural and synthetic salts melted at 240–241°, as did a mixture of the two. ***l*-Sparteine dipicrate,** yellow needles, m. p. 207–208°, was prepared directly from the *d*-β-camphorsulfonate salt in ethanol by the addition of ethanolic picric acid (*Anal.* Calcd. for $C_{27}H_{32}N_8O_{14}$: C, 46.82; H, 4.66; N, 16.18. Found: C, 47.13; H, 4.54; N, 15.94). The melting point was depressed when the compound was mixed with *dl*-sparteine dipicrate, m. p. 208°, undepressed when mixed with natural *l*-sparteine dipicrate, m. p. 208°.[4]

Following the separation of the *l*-sparteine *d*-β-camphorsulfonate, *d*-sparteine-enriched base was freed from the mother liquor and was converted, by treatment with *l*-β-camphorsulfonic acid,[5] to ***d*-sparteine *l*-β-camphorsulfonate.** After three recrystallizations from acetone, this salt melted at 239–241° and exhibited a specific rotation, $[\alpha]^{22}\text{D}$ −24.0 ± 0.5° (*C*, 2.040 in chloroform), approximately equal and opposite to that of its antipode. ***d*-Sparteine dipicrate,** yellow needles, m. p. 208–209°, was prepared directly from the *l*-β-camphorsulfonate salt and showed no depression in melting point when mixed with the dipicrate of natural *d*-sparteine,[6] m. p. 208°.[7] ***d*-Sparteine monoperchlorate,** colorless needles, m. p. 174°, was prepared by dissolving *d*-sparteine *l*-β-camphorsulfonate in a small amount of water, acidifying to *p*H 1–2 with 65% perchloric acid, and then basifying with ammonium hydroxide. The perchlorate separated on cooling and was recrystallized from ethanol-ether. A mixture with the monoperchlorate of natural *d*-sparteine,[6] m. p. 173°,[7] was also 173°.

The infrared absorption spectra of natural *l*-, resolved *l*-, natural *d*-, and resolved *d*-sparteine dipicrates were determined[8] and were found to be identical for these samples in the crystalline state and very slightly different from that of crystalline *dl*-sparteine dipicrate.[3]

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NELSON J. LEONARD
ROGER E. BEYLER

RECEIVED JANUARY 14, 1949

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(1) Clemo, Raper and Short, *Nature*, **162**, 296 (1948).

(2) Sorm and Keil, *Coll. Czechoslov. Chem. Commun.*, **13**, 544 (1948).

(3) Leonard and Beyler, THIS JOURNAL, **70**, 2298 (1948).

(4) Moureu and Valeur, *Bull. soc. chim.*, [3] **29**, 1135 (1903).

(5) Obtained by resolution of *dl*-β-camphorsulfonic acid according to the method of Burgess and Gibson, *J. Soc. Chem. Ind.*, **44**, 496T (1925).

(6) We wish to acknowledge the kindness of Dr. Léo Marion, National Research Council, Ottawa, Canada, in supplying us with authentic samples of *d*-sparteine dipicrate and *d*-sparteine perchlorate.

(7) Marion and Ouellet, THIS JOURNAL, **70**, 691 (1948); Marion and Turcotte, *ibid.*, **70**, 3253 (1948); Marion and Cockburn, *ibid.*, **70**, 3472 (1948).

(8) The authors are indebted to Mrs. James L. Johnson for determination of the infrared absorption spectra.

CRYSTALLINE XYLAN AND MANNAN

Sir:

I wish to report the isolation of a crystalline xylan from barley straw and birchwood. The weaker linkages of the xylan-rich fraction of the hemicelluloses of these materials, purified by the method of Salkowski, were hydrolyzed under mild conditions (0.2% oxalic acid at 100°); the reducing value of the hydrolysate was virtually constant after five hours. The insoluble portion from the hydrolysis, on autoclaving at 120°, was soluble in water to the extent of about 0.2%; on cooling to 60–70°, hexagonal platelets with rounded corners separated. The xylan was purified by heating a water paste for five hours at 120°, readily filterable spherocrystals being obtained. Barley xylan is purified more readily than birch xylan. Aging of the amorphous xylan or contact with dilute alkali renders it insoluble in 3 *N* sodium hydroxide. Wet heat at 120° and *p*H 5 restores its solubility. Attempts to prepare a slash pine xylan failed. The crystals are doubly refractive and give typical crystalline X-ray diffraction patterns. Crystalline D-xylose was prepared in good yield and its identity confirmed. A diphenylhydrazine test for arabinose in the mother liquor was negative. This, coupled with the high pentosan analysis, indicates relatively pure xylan. Breddy–Jones and Wise–Appling xylose determinations on 3% nitric acid hydrolysates confirmed this finding. Osmotic pressure measurements on methylated barley xylan indicate a degree of polymerization of 39. A newly developed aldose end-group method gave the

	Material from selective hydrolysis		Repeatedly recrystallized xylan	
	Barley	Birch	Barley	Birch
Pentosans as xylan (cor. for uronic acids), %	97.4	92.4	99.5	97.9
Uronic anhydride (cor. for CO_2 from xylose), %	2.4	6.4	0.38	2.39
Ash, %	0.85	..	0.34	0.39

same value. Birch xylan, compared viscometrically with barley xylan, had a degree of polymerization of 35. Optical rotational measurements indicate a 1,4′,β-linkage. This is based on the rotational shift method of Reeves and comparisons with Haworth's esparto xylan.

Mannan "A" of ivory nut readily forms supersaturated solutions of 1% concentration. Such a solution crystallizes if heated to 60–70° for several days. The crystals initially are rods and gradually become dumb-bell shaped as growth continues. Slight double refraction is evident. A mannan-rich fraction from slash pine gave similar crystals. Repeated recrystallization did not alter the facility or habit of crystallization. The crystals assayed only 50% mannan and had a light tan color.

This work will be published in full at a later date.

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN ALBERT P. YUNDT

RECEIVED JANUARY 15, 1949

THE STRUCTURE OF PATULIN

Sir:

We are reporting elsewhere in detail the considerations which led us to reject the accepted structure[1] (I, *and/or* tautomers) for the well-known mold metabolite and antibiotic, patulin, in favor of a new expression (II, R = OH). Here we record the synthesis of (II, R = H), which we designate as *desoxypatulin,* since its relevant physical properties resemble those of patulin so closely as to provide very strong support for our structural views.

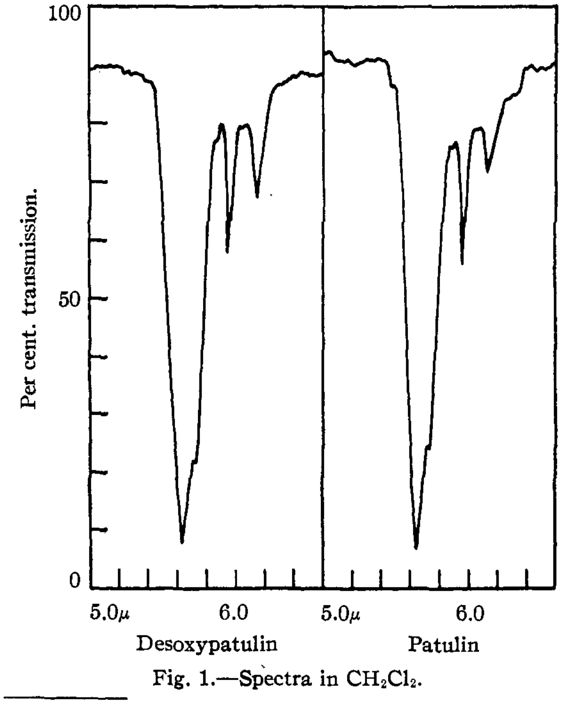
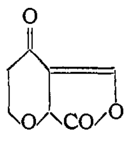


Fig. 1.—Spectra in CH_2Cl_2.



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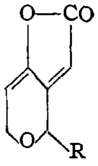
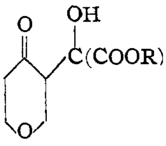
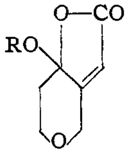


II

Condensation of tetrahydro-γ-pyrone with ethyl mesoxalate gave the ketol (III, R = Et), m. p. 58.5–60° (Calcd. for $C_{12}H_{18}O_7$: C, 52.55; H, 6.57. Found: C, 52.73; H, 6.67). When the corresponding acid (III, R = H) was heated with acetic anhydride and acetic acid, among the products obtained were: (i) the *cis*-acid (IV, R = H), m. p. 122–123° (Calcd. for $C_7H_8O_4$: C, 53.85; H, 5.13. Found: C, 53.77; H, 5.18), (ii) the lactol acetate (IV, R = Ac), m. p. 121.5–123° (Calcd. for $C_9H_{10}O_5$: C, 54.55; H, 5.05. Found: C, 54.64; H, 5.02), (iii) the *trans*-acid (V), m. p. 153° (Calcd. for $C_7H_8O_4$: C, 53.85; H, 5.13. Found: C, 53.89; H, 5.25). Treatment of (IV, R = Ac) with warm acetic anhydride–acetic acid–sulfuric acid[2] gave desoxypatulin (II, R = H), m. p. 46–48° (Calcd. for $C_7H_6O_3$: C, 60.80; H, 4.35. Found: C, 60.62; H, 4.37), whose ultraviolet spectrum possessed a single maximum at 273 mμ (log ε, 4.17) (patulin: $\lambda_{max.}$, *276 mμ (log ε, 4.22)*), and whose infrared spectrum in the double bond region reproduced in detail the very characteristic spectrum of patulin in the same region (Fig. 1).



III



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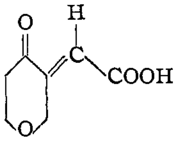
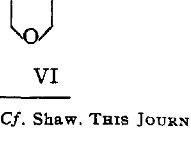
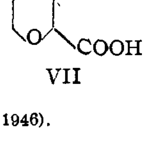


V

Further support for the structure (II, R = OH) was forthcoming when the oily acid (VI), obtained by the hydrogenation either of the *cis*-acid (IV, R = H) or the *trans*-acid (V), was shown to be identical, through comparison of the methyl ester 2,4-dinitrophenylhydrazones, m. p. 149–150°, with the acid $C_7H_{10}O_4$ originally obtained by Ber-



VI



VII

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[1] For references *cf. Quart. Reviews Chem. Soc.*, **2**, 53 (1948).

[2] *Cf.* Shaw, THIS JOURNAL, **68**, 2510 (1946).