

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, $[\alpha]^{20}_D 24.8 \pm 0.5^\circ$ (C, 1.932 in chloroform), and consistent with that of an authentic sample of the *d*- β -camphorsulfonate of natural *l*-sparteine, $[\alpha]^{20}_D 24.4 \pm 0.5^\circ$ (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, $[\alpha]^{20}_D -24.0 \pm 0.5^\circ$ (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 pH 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 determined⁸ 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

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

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RECEIVED JANUARY 14, 1949

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 pH 5 restores its solubility. Attempts to prepare a slash pine xylan failed. The crystals are doubly

	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

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

(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).