pirated, and the residue crystallized from 30 ml. of 95% ethanol, yielding 0.37 g. (58%) of pale yellow needles, m.p. 172–174° dec. This material decolorized cold 2% permanganate solution. The analytical sample was prepared by recrystallization from absolute alcohol.

Anal. Calcd. for $C_{14}H_{15}ClN_2O_6S$: C, 44.86; H, 4.03; Cl, 9.46. Found: C, 44.80; H, 4.30; Cl, 9.29.

Attempted Preparation of 6-Chloro-3,4-dimethyl-Δ^3-cyclohexenyl 2′,4′-Dinitrophenyl Sulfide.—To a solution of 0.50 g. of II (R = H), in 25 ml. of benzene, was added 5 ml. 2,3-dimethyl-1,3-butadiene and the solution was refluxed 49 hours. Solvent and excess diene were aspirated, and the residue crystallized from carbon tetrachloride, giving 0.42 g. of orange needles, m.p. 129–131°. The mixed melting point with authentic starting material (m.p. 130–131°) was 129–131°. From the mother liquor, 0.05 g. more of material was recovered; total recovery 94%.

Treatment of II (R = C_6H_5) with Raney Nickel.—A solution of 1.50 g. (0.0036 mole) of 2-chloroethenyl 2′,4′-dinitrophenyl sulfide (II, R = phenyl),[2] in 75 ml. of absolute ethanol was refluxed with *ca.* 15 g. of Raney nickel for 1.5 hours. About 5 g. more of catalyst was added, and reflux continued for 1.5 hours. The mixture was filtered through diatomaceous earth, and the catalyst residue washed with two 25-ml. portions of boiling absolute ethanol. The washings were added to the filtrate, which was then concentrated in an air stream to about 100 ml. The solution became dark during this treatment, but was decolorized by adding 10 ml. of 6 *N* hydrochloric acid. Evaporation was continued almost to dryness, 25 ml. of water was added, and the precipitated solid removed by suction filtration. After washing with three 10-ml. portions of water, the solid was dried *in vacuo* and weighed 0.51 g. (100%). Decolorization with charcoal and crystallization from aqueous ethanol gave excellent, colorless plates melting at 48.5–49.5°. The Beilstein test for halogen was negative, and a mixed melting point with authentic 1,2-diphenylethane (m.p. 49–50°), prepared from stilbene, was 48.5–49.5°.

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Occurrence of Some Simple Sugars in Heartwood of Port Orford Cedar (*Chamaecyparis lawsoniana*)

BY GENE KRITCHEVSKY AND ARTHUR B. ANDERSON

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Free arabinose and glucose appear to be common constituents in a great variety of both the heartwood and sapwood of the genus *Pinus*.[1] Aside from the isolation of L-arabinose from the heartwood of western red cedar (*Thuja plicata*),[2] very little appears to be known relative to the nature of some of the simple free carbohydrates present in the wood of various genera other than the *Pinus* species.

While investigating the water-soluble extract from Port Orford cedar heartwood (*Chamaecyparis lawsoniana*), a yield of 0.74 g. of a pentose sugar, identified as L(+)-arabinose was obtained from 500 g. of wood. This was the only sugar which was isolated in crystalline form. However, when the concentrated aqueous extract was submitted to paper partition chromatography, in addition to arabinose, the chromatograms showed R_f values which confirmed the presence of galactose, glucose and xylose. This appears to be the first report on the nature of some of the simple free sugars present in the genus *Chamaecyparis*.

Experimental

A composite sample of 500 g. of Port Orford cedar heartwood sawdust from five stumps was extracted in a glass percolator with five successive 1-liter portions of water at room temperature. The combined aqueous extract was concentrated on a water-bath at 40° and 18 mm. to 10 ml., then filtered to remove insoluble material. Approximately 1% of the filtrate was reserved for chromatographic analysis. The remainder of the filtrate was evaporated to dryness and the residue recrystallized from methanol, yielding 0.74 g. of a white crystalline product, m.p. 154–156° (0.15% yield based on the weight of wood used). Further recrystallization from hot methanol raised the m.p. to 159.3–160.2°, with an initial specific rotation of +136° (2% in water), and an equilibrium value of +104°. No change in melting point with an authentic sample of L(+)-arabinose with specific equilibrium rotation of +105.5°. A *p*-nitrophenyl hydrazone was prepared with m.p. 179.4–180°; mixed melting point with authentic phenylhydrazone derivative unchanged.

Paper chromatograms were run according to the method described by Partridge[3] on a portion of the above concentrated aqueous extract using four separate solvent mixtures. These solutions consisted of (1) ethyl acetate–pyridine–water (2–1–2),[4] (2) *sym*-collidine saturated with water,[5] (3) *n*-butyl alcohol–acetic acid–water (4–1–5)[5] and (4) isobutyric acid–water (4–1). Each of the chromatograms was run on a Whatman paper No. 1 (8 cm. × 57 cm.) using galactose, glucose, arabinose and xylose as the reference mixture. A chromogenic spraying agent of aniline oxalate[3] was used, which gives brown spots for the hexoses and pink spots for the pentoses.

R_f VALUES OBTAINED WITH EACH OF THE FOUR CHROMATOGRAMS

Solvent used	R_f values: Galactose	Glucose	Arabinose	Xylose	
Ethyl acetate–pyridine–water (2–1–2)	0.24	0.29	0.34	0.38	reference
	.24	.29	.34	.38	aq. extract
sym-Collidine satd. with H_2O	.35	.40	.44	.53	reference
	.35	.40	.44	.52	aq. extract
n-Butyl alcohol–acetic acid–water (4–1–5)	.16	.18	.22	.28	reference
	.16	.18	.22	.28	aq. extract
Isobutyric acid–water (4–1)	.14	.14	.19	.19	reference
	0.14		0.19		aq. extract

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The Site of Enzymatic Hydrogen Transfer in Diphosphopyridine Nucleotide[1]

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In a study of a model reaction for pyridine nucleotide dehydrogenases, Mauzerall and Westheimer[2] have shown that 1-benzyl-4-deuteriodihydronicotinamide transfers D to malachite green, whereas the 2-deuterio and 6-deuterio isomers do not. Their conclusion regarding the site of the reduction of the N-substituted nicotinamide was in agreement with the previous conclusions of Colowick and his collab-

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(2) D. Mauzerall and F. H. Westheimer, THIS JOURNAL, **77**, 2261 (1955).