spectively, in the relation $K'_{a_2} = K'_{a_A} + K'_{a_B}$ yields 8.39 as the pK'_{a_2} of cysteine. This is in fairly good agreement with the value 8.30 which we measure experimentally under the same conditions (Table I). From $K'_{a_C} = K'_{a_2}K'_{a_3}/K'_{a_A}$ we find pK'_{a_C} to be 10.05 and from $K'_{a_D} = K'_{a_2}K'_{a_3}/K'_{a_B}$ the figure for pK'_{a_D} is 9.95. The somewhat smaller values of K'_{a_C} and K'_{a_D} reported by Ryklan and Schmidt[6] are a consequence of the higher value which they selected for the pK'_{a_3} of cysteine, 10.78[13] at zero ionic strength. In any event, both K'_{a_C} and K'_{a_D} would be anticipated to be small because of the weakening effect of the net negatively charged intermediate ion species. The individual constants calculated as above give a ratio of *zwitterion form/neutral uncharged form* of 1.3:1, neglecting the full negative charge of the carboxyl group.

Our results support the concept that the acidic strength of the $-SH$ and $-NH_3^+$ groups of cysteine are almost identical. These data are therefore in agreement with the ionization scheme proposed by Edsall.[4]

Acknowledgment.—The authors are indebted to Dr. J. T. Edsall for advice and criticism. This research was supported in part by a grant-in-aid from the American Cancer Society upon recommendation of the Committee on Growth of the National Research Council.

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Derivatives of Sulfenic Acids. XXI. Some Reactions of β-Chlorovinyl 2,4-Dinitrophenyl Sulfides[1]

BY NORMAN KHARASCH AND STEVEN J. ASSONY

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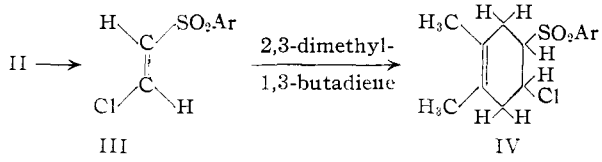
Incidental to other studies, it was of interest to examine the oxidation and catalytic desulfuration of certain β-chlorovinyl 2,4-dinitrophenyl sulfides (II, $R(Cl)C{=}C(R){-}SC_6H_3(NO_2)_2$) which result by adding 2,4-dinitrobenzenesulfenyl chloride (I) to symmetrical alkynes.[2] The results of these reactions and some related observations are reported now.

The adducts (II, R = H, C_6H_5, CH_3 and C_2H_5) did not respond to the usual unsaturation test with bromine in carbon tetrachloride, showing the combined effects which the chlorine and 2,4-dinitrophenylthio groups in these substances exert in lowering the reactivity of the olefin positions to electrophilic attack by bromine. This suggested the possibility that the adducts might be preferentially oxidizable to vinyl sulfones and this was shown to be so for II (R = H), which gave the corresponding 2-chlorovinyl 2′,4′-dinitrophenyl sulfone (III) in 75% yield using hydrogen peroxide in glacial acetic acid. The presence of the double bond in III was demonstrated by forming the Diels–Alder product IV, from III and 2,3-dimethyl-1,3-butadiene.[3] In analogy with evidence[4] which shows that I adds to olefins to give the *trans* adducts, the *trans* arrangement of Cl and $-SAr$ (Ar = 2,4-dinitrophenyl) in II, and of Cl and $-SO_2Ar$ in III and IV, is most likely.



Dienophiles similar to III have been recorded previously[5-7] but the inclusion of both the chloro and sulfone functions is unique to III. In contrast, attempts to add II (R = H or C_6H_5) to 2,3-dimethyl-1,3-butadiene, under conditions used to prepare IV, were not successful.

Treatment of the sulfenyl chloride–diphenylacetylene adduct (II, R = phenyl)[2] with Raney nickel, under typical desulfurating conditions, caused desulfuration, dehalogenation and hydrogenation, giving quantitative conversion to 1,2-diphenylethane.

By proving the presence of the olefin bond, in the case of II (R = H), and by showing that no rearrangements of the carbon chain are involved in the addition of I to diphenylacetylene, the above results—aside from their synthetic interest—also support the structures assigned[2] to the various examples of II.

Experimental[8]

2-Chloroethenyl 2′,4′-Dinitrophenyl Sulfone.—A solution of 0.50 g. (0.0019 mole) of the sulfide (II, R = H) and 5 ml. of 30% hydrogen peroxide in 25 ml. of glacial acetic acid was warmed on the steam-bath for 15 minutes, then left overnight at room temperature. The solution was warmed for two more hours, residual peroxides were decomposed catalytically with platinum wire, and water was added to the hot solution until it became turbid. Pale yellow, feathery plates (0.42 g., 75%), m.p. 114–120°, deposited on standing. The analytical sample was recrystallized from carbon tetrachloride and melted at 122–123°, with prior sintering from 116°.

Anal. Calcd. for $C_8H_5ClN_2O_6S$: C, 32.83; H, 1.72. Found: C, 32.91; H, 1.90.

The product decolorized permanganate in acetone instantaneously, but failed to react with bromine in carbon tetrachloride even at the boiling point of the solvent. In contrast (II, R = H) decolorized permanganate in acetone only slowly and reacted slowly with bromine in carbon tetrachloride, with evolution of hydrogen bromide.

6-Chloro-3,4-dimethyl-Δ³-cyclohexenyl 2′,4′-Dinitrophenyl Sulfone(IV).—Sulfone III (0.50 g., 0.0017 mole) and 5 ml. of 2,3-dimethyl-1,3-butadiene were refluxed in 30 ml. of benzene for 48 hours. Solvent and excess diene were as-

(1) This study was carried out under sponsorship of the Office of Ordnance Research, United States Army, Contract DA-04-495-Ord. 306.

(2) N. Kharasch and S. J. Assony, THIS JOURNAL, **75**, 1081 (1953).

(3) The infrared spectra of each of the adducts, II, were examined, but a simple assignment to the double bond could not be made because of related absorptions in these complicated molecules. These spectra will be reported, together with a series of related compounds, in a separate manuscript.

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(6) H. R. Snyder and D. P. Hallada, THIS JOURNAL, **74**, 5595 (1952); H. R. Snyder, H. N. Anderson and D. P. Hallada, *ibid.*, **73**, 3258 (1951).

(7) C. S. Rondestvedt and J. C. Wygant, *ibid.*, **73**, 5785 (1951).

(8) The microanalyses were made by Mr. W. J. Schenck. Melting points are not corrected.

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]

BY FRANK A. LOEWUS, BIRGIT VENNESLAND AND DANIEL L. HARRIS

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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-

(1) This investigation was supported in part from grants from the National Institutes of Health, United States Public Health Service, and by the Dr. Wallace C. and Clara A. Abbott Memorial Fund of the University of Chicago.

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