(3) to 4 and 5.—A solution of 2.70 g (0.0141 mol) of 3 ($[\alpha]^{25}D$ +5°) in 500 ml of 2 *N* ammonium hydroxide was allowed to stand 5 days at 25° and the products were isolated as before. Yields of 492 mg (18.2%) of isomer 4 and 370 mg (11.5%) of 5 hydrochloride were obtained.

Oxidation of Sulfoxides 4 and 5 to the Corresponding Sulfones 7 and 9.—A solution of 700 mg (0.00366 mol) of 5 in 120 ml of 0.25 *N* sulfuric acid was oxidized with 464 mg of potassium permanganate. After removal of sulfate and manganese dioxide and purification with a cation exchanger, a yield of 312 mg of **3-(*R*)-carboxy-5-(*R*)-ethyl-1,4-thiazane S-dioxide** (9) was obtained, identified by ir and nmr.

Oxidation of a sample of 4 (200 mg) in a similar manner yielded 70 mg of **3-(*R*)-carboxy-5-(*S*)-ethyl-1,4-thiazane S-dioxide** (7), established by ir.

Reduction of Sulfoxide 4 to Sulfide 6.—Hydriodic acid reduction of 1.30 g (0.0057 mol) of 4 HCl gave 902 mg (89%) as the free amino acid. Recrystallization from water–ethanol (1:4) yielded pure **3-(*R*)-carboxy-5-(*S*)-ethyl-1,4-thiazane** (6) as large lathlike crystals: mp 256 dec; ir, no sulfoxide absorption; $[\alpha]^{26}D$ −58.8° (*c* 2, water), $[\alpha]^{25}D$ −33.8° (*c* 2.5, 1 *N* hydrochloric acid).

Anal. Calcd for $C_7H_{13}NO_2S$: C, 47.97; H, 7.48. Found: C, 47.8; H, 7.31.

Reduction of Sulfoxide 5 to Sulfide 8.—A sample of 1.496 g (0.00782 mol) of 5 was reduced and the product was crystallized from water–ethanol (1:5) to yield the sulfide, **3-(*R*)-carboxy-5-(*R*)-ethyl-1,4-thiazane** (8) (77%), as rectangular prisms: mp 275–277° dec (phase change above 230°, prisms → needles); sulfoxide absent by ir; $[\alpha]^{25}D$ −82.5° (*c* 1.8, water), −61.07° (*c* 2.2, in 3 *N* hydrochloric acid).

Anal. Calcd for $C_7H_{13}NO_2S$: C, 47.97; H, 7.48; N, 7.99. Found: C, 48.0; H, 7.45; N, 7.98.

Registry No.—2, 19206-35-0; 3, 19206-36-1; 4, 19206-37-2; 4 HCl, 19206-38-3; 5, 19206-39-4; 6, 19206-40-7; 8, 19206-41-8.

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The Reductic Acid-^{14}C Derived from D-Xylose-1-^{14}C and 2-Furaldehyde-α-^{14}C[1,2]

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In addition to its formation from hexuronic acids and polyuronides, reductic acid (2,3-dihydroxy-2-cyclopenten-1-one) has been reported to be formed from both D-xylose[3] and its structurally related dehydration product, 2-furaldehyde.[4] Subsequent to these reports, several investigators[5–7] have attempted to explain the mechanism of formation of this compound from both D-xylose and 2-furaldehyde, and, in all cases, these suggestions predict that C-1 of D-xylose and the α-carbon atom of 2-furaldehyde should ultimately reside at C-2 of reductic acid.

TABLE I

% DISTRIBUTION OF ISOTOPE IN REDUCTIC ACID-^{14}C

Source	C-2[a]	C-1 and C-3[b]	C-4 and C-5[b]
D-Xylose-1-^{14}C	58.8	41.2	0.3
2-Furaldehyde-α-^{14}C	57.0	42.0	1.0

[a] Determined by difference after conversion of reductic acid-^{14}C into succinic acid-^{14}C. [b] Determined by difference after the conversion of succinic acid-^{14}C into ethylene diamine *via* a Curtius degradation.

In this work, some yield figures and structural relationships between reactants and product were determined using D-xylose-1-^{14}C and 2-furaldehyde-α-^{14}C as starting materials in the conversion. The former compound was obtained commercially and the latter was prepared from D-xylose-1-^{14}C, a conversion which is known[8] to give 2-furaldehyde exclusively labeled at the α-carbon atom. These compounds were converted into reductic acid at 150° in 5% sulfuric acid in low yield (0.24% in the case of D-xylose, calculated from isotope dilution figures). Structural relationships were investigated by systematic degradation of the reductic acid-^{14}C obtained from these precursors. Conversion of reductic acid into succinic acid allowed a determination of the radiochemical activity present at C-2 of reductic acid and since, in the reductic acid molecule, the oxygen-bearing carbon atoms 1 and 3 are equivalent as are the methylene carbon atoms 4 and 5 and are represented by, respectively, the carboxyl carbon atoms and the methylene carbon atoms of succinic acid, a determination of the specific activity of the ethylene diamine derived from succinic acid of known activity *via* a Curtius degradation allowed the determination of the radiochemical activity residing in both pairs of carbon atoms. Degradation of the reductic acid-^{14}C obtained from either D-xylose-1-^{14}C or 2-furaldehyde-α-^{14}C gave identical results (Table I) with about 60% of the activity at C-2 and 40% at C-1 and C-3. In both cases, negligible activity was found in the methylene carbon atoms 4 and 5.

The identical label distribution in the reductic acid indicates a common primary source and suggests that it is 2-furaldehyde derived, since the latter is readily formed from D-xylose under the conditions of formation of reductic acid. That pentoses are sources of reductic acid has been widely accepted exclusively on the basis of the experimental findings of Reichstein and Oppenauer[3] who reported its isolation, in crystalline form, in about 0.5% yield starting from D-xylose.

In a recent study of the formation of reductic acid from D-galacturonic acid,[9] it was found that, in 90% of the reaction product, C-1 of the uronic acid corresponded to C-2 of reductic acid, indicating that this fraction of the product arose in a manner consistent with mechanism proposals on this subject.[5–7] In 10% of the product, however, C-1 of the uronic acid was found at C-1–C-3 of reductic acid and represented an un-

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explained reaction pathway. Since, at the reaction conditions used, considerable 2-furaldehyde is evolved from uronic acids, it must also contribute to product formation in this reaction. Assuming that all of the reductic acid labeled at C-1–C-3 formed during uronic acid decomposition is 2-furaldehyde derived and using the radioisotopic label distribution figures obtained herein, it can be concluded that, of the reductic acid-^{14}C formed from D-galacturonic acid-1-^{14}C, all of the C-1–C-3-labeled product and 15% of the C-2-labeled product are derived from 2-furaldehyde. The remaining 75%, labeled exclusively at C-2, must be formed by a mechanism unique to hexuronic acids.

Experimental Section

Materials and Methods.—Specific activities of labeled compounds were determined on a Model No. 3003 Packard Tricarb spectrometer using an internal toluene-^{14}C standard. D-Xylose-1-^{14}C was obtained from CalBiochem, Los Angeles, Calif. Radiochemically inert reductic acid was prepared from pectin as described in a previous report[9] and had mp 211–212°, λ_{max} 267 mμ (ϵ 13,300) (95% ethanol). Thin layer chromatography was performed on silica gel GF coated glass plates and spots were detected with either aniline hydrogen phthalate spray reagent or uv irradiation.

Reductic Acid-^{14}C From D-Xylose-1-^{14}C.—To an 8-mm pyrex glass tube was added 25 μCi of D-xylose-1-^{14}C (200 mg) and 1.0 ml of 5% sulfuric acid. The tube was sealed and heated at 150° for 2 hr and the contents were then transferred to a beaker and neutralized with barium carbonate. The resulting solution, after filtration through Celite, was passed through a column of Dowex 50 (hydrogen form) and evaporated to dryness. Thin layer chromatograms of the residue using chloroform–acetic acid (9:1) as irrigant indicated that reductic acid was the major product. To the residue was added 1.50 g of radiochemically inert reductic acid and the sample was recrystallized from N,N-dimethylformamide: yield 1.37 g. The resulting crystals were sublimed five times at 140° (0.1 mm), whereupon a constant specific activity of 4.20×10^{-3} μCi/mmol was attained.

Reductic Acid-^{14}C from 2-Furaldehyde-α-^{14}C.—The 2-furaldehyde-α-^{14}C used in this experiment was prepared essentially by the method described by Hughs and Acree.[10] To 750 ml of 5.0 *N* sulfuric acid was added 75 μCi (3.0 g) of D-xylose-1-^{14}C and the solution was slowly distilled. At the end of 6 hr, 250 ml of distillate (containing the 2-furaldehyde-α-^{14}C) was collected. This solution was made 5% in sulfuric acid and was heated 1.5 hr at 150° in a glass-lined Parr bomb. Reductic acid was qualitatively detected, isolated, and purified as described above with 3.0 g of inert reductic acid being used as diluent. The pure product (2.0 g) had a specific activity of 1.98×10^{-3} μCi/mmol.

Chemical Degradation of the Reductic Acids-^{14}C.—A 1.2-g sample of reductic acid-^{14}C (specific activity 4.20×10^{-3} μCi/mmol) derived from D-xylose-1-^{14}C was converted into succinic acid by permanganate oxidation as described in a previous report.[9] After recrystallization from water, the succinic acid (mp and mmp 182°) had a specific activity of 1.74×10^{-3} μCi/mmol. This material (500 mg) was subjected to a Curtius degradation as described by Benson and Bassham[11] to give crystalline ethylenediamine dihydrochloride (mp and mmp 203°) having a specific activity of 1.40×10^{-5} μCi/mmol. Repetition of the above experiments using 2-furaldehyde-α-^{14}C derived reductic acid-^{14}C (specific activity 1.90×10^{-3} μCi/mmol) gave succinic acid having a specific activity of 0.82×10^{-3} μCi/mmol and subsequently, ethylenediamine dihydrochloride having a specific activity of 2.2×10^{-5} μCi/mmol.

Registry No.—2,3-Dihydroxy-2-cyclopenten-1-one-2-^{14}C, 19214-81-4; D-xylose-1-^{14}C, 19588-10-4; 2-furaldehyde-α-^{14}C, 19238-30-3.

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Rearrangement of Azidoquinones. III. Reaction of 1,4-Benzoquinone with Sodium Azide

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In 1915, Oliveri-Mandalá and Calderao[1,2] showed that 1,4-benzoquinone reacts with hydrazoic acid in benzene to give 2-azido-1,4-benzohydroquinone (**1**). Twenty years later Fieser and Hartwell[3] obtained an azidohydroquinone, believed to be the same as that reported in the earlier work,[1,2] when an acetic acid solution of 1,4-benzoquinone was treated with sodium azide. We have reinvestigated this latter reaction and find the product to be 2,5-diazido-1,4-benzohydroquinone (**2**). The structure of **2** is based upon its spectral properties and upon its conversion into a diacetate (**3**), 2-amino-5-azido-1,4-benzoquinone (**4**), 2,5-diamino-1,4-benzoquinone (**5**), and the γ-cyanomethylene-$\Delta^{\alpha,\beta}$-butenolide (**6**).

Addition of excess sodium azide to an acetic acid solution of 1,4-benzoquinone resulted in a mildly exothermic reaction followed by the precipitation of diazide **2** in 33% isolated yield. The nmr spectrum of this *highly explosive* compound is consistent for the diazide structure, showing only one sharp singlet at δ 6.53 for the two equivalent aromatic protons. The ir spectrum of **2** shows characteristic absorptions for the phenolic hydroxyl and azide groups at 3300 and 2120 cm^{-1}, respectively. The hydroquinone structure was confirmed by the formation of a diacetate derivative, **3**, in 92% yield when **2** was treated with acetic anhydride. The spectral (nmr, ir, and mass spectrum) properties and combustion analysis of **3** are in agreement with its formulation. This diacetate is a relatively stable compound, melting with decomposition at 160–161°. The diacetate reported by Oliveri-Mandalá and Calderao[2] for monoazidehydroquinone **1** melted from 115 to 120° and decomposed at 140°.

These data, although consistent for **2** as the structure of the diazidohydroquinone, do not rule out other possible formulations, particularly with regard to the orientation of the two azide substituents. In order to establish this relationship, diazide **2** was converted into a known compound, 2,5-diamino-1,4-benzoquinone[4] (**5**) and to γ-lactone **6** (Scheme I). The key intermediate in both of these transformations is 2-amino-5-azide-1,4-benzoquinone (**4**). We have previously shown[5] that azidohydroquinones readily disproportionate to give aminoquinones and, when this reaction was applied to the azidohydroquinone, **2**, the required 2-amino-5-azido-1,4-benzoquinone (**4**) was obtained in 75% yield. The nmr spectrum of **4** strongly indicates that the azido and amino groups are in the 2 and 5 positions since the

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