assignment of the doublet of doublets at τ 7.66 (J = 14, 2 Hz) to the C-14 proton. Then irradiation of the latter peaks caused not only the collapse of the doublet at τ 3.52, but also sharpening of a broad singlet at τ 6.18 assigned to the C-12 proton. The long-range coupling between the C-12 and C-14 protons is in accord with an α configuration for the C-12 hydroxyl. The small coupling between the C-11 and C-12 protons suggests a β stereochemistry for the C-11 hydroxyl, since any flattening of the ring to relieve the strain caused by two axial hydroxyls could cause the dihedral angle between the C-11 and C-12 protons to approximate 90°.

A broad multiplet at τ 5.3, superimposed on two other proton resonances, was assigned to the C-11 proton. Addition of benzene to the chloroform solution of 1 resolved the three resonances into the C-11 proton multiplet, a doublet (J = 8 Hz) coupled with a broadened doublet at τ 6.43, both assigned to the C-30 protons, and a triplet (J = 3 Hz) assigned to the C-7 proton. Irradiation of the C-11 proton multiplet caused the collapse of an OH doublet (J = 7 Hz) at τ 6.82 as well as change in a signal at τ 7.8. The latter signal was assigned to the C-9 proton.

The uv spectrum and characteristic fragment ion[8] at m/e 151 in the mass spectrum of quassimarin (1) supported the formulation of the A-ring portion as shown. In addition, the NMR spectrum of 1 contained signals for a vinyl proton and a vinyl methyl as well as a sharp singlet at τ 5.83 assignable to the C-1 proton. The detection of a 6% nuclear Overhauser effect between the C-1 and C-9 protons confirmed the β stereochemistry of the C-1 hydroxyl.

Experimental Section

General. Melting points were determined on a Mettler Model FP2 hot stage and are uncorrected. Ultraviolet absorption spectra were determined on a Beckman Model DK-2A recording spectrophotometer. Infrared spectra were determined on Perkin-Elmer Model 257 and Model 337 recording spectrophotometers. Nuclear magnetic resonance spectra were determined on a Varian HA-100 spectrometer or a JEOL PS-100 pulsed FT NMR spectrometer interfaced to a Texas Instrument JEOL 980A computer, with tetramethylsilane as an internal standard. Mass spectra were determined on Hitachi Perkin-Elmer Model RMU-6E and AEI Model MS-902 spectrometers. Values of $[\alpha]$D were determined on a Perkin-Elmer Model 141 automatic polarimeter. Gas–liquid chromatography was carried out on a Varian Aerograph Model 1800 gas chromatograph equipped with a 9-ft column, packed with 18% QF on Chromosorb W, at a column temperature of 80 °C with helium as carrier gas. Microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich. Petroleum ether refers to the fraction of bp 60–68 °C. All thin layer chromatography was carried out on ChromAR 7GF precoated glass plates (Mallinckrodt). Visualization of TLC was effected with short-wavelength uv and concentrated sulfuric acid–vanillin–ethanol (20:1:3) spray.

Extraction and Preliminary Fractionation. The dried sap (2 kg) of *Q. amara* was partitioned between water (12 l.) and ethyl acetate (3 × 8 l.). The combined ethyl acetate layers were evaporated to give a dark brown residue (A, 80 g). Fraction A was partitioned between 10% aqueous methanol (0.5 l.) and petroleum ether (5 × 0.3 l.). The aqueous methanol layer and combined petroleum ether layers were evaporated to give B (77 g) and C (3 g), respectively. Further partitioning of fraction B between 20% aqueous methanol (0.6 l.) and carbon tetrachloride (3 × 0.3 l.) afforded, after evaporation, fractions D (65 g) and E (12 g).

Fraction D was subjected to column chromatography (SilicAR CC-7, 1500 g) with chloroform followed by chloroform containing increasing amounts of methanol as eluents. Elution with 2% methanol in chloroform gave fraction F (6.1 g) which was further fractionated by column chromatography on silica gel 60 (500 g). Elution with 4% isopropyl alcohol in dichloromethane yielded fraction G (1.9 g). Fraction G was submitted to further column chromatography on SilicAR CC-7 (120 g). Elution with 25% acetone in hexane gave fractions H (0.33 g) and I (0.49 g).

Simalikalactone D (2). Fraction H was purified by preparative TLC on ChromAR using ethyl acetate–cyclohexane (2:1). Elution of the major uv-active band afforded a residue which gave needles upon crystallization from ethyl acetate–hexane (**2**, 0.089 g, 0.005%). The material was identified by comparison of its melting point, $[\alpha]$D, and uv and NMR spectra with those reported for simalikalactone D,[6] and by comparison of its TLC and ir and mass spectra with those of an authentic sample.[9]

Quassimarin (1). Preparative TLC of fraction I on ChromAR using ethyl acetate–cyclohexane (2:1), followed by elution of the major uv-active band, gave a residue which crystallized as needles from ethyl acetate–hexane (**1**, 0.06 g, 0.003%): mp 237.5–238.5 °C dec; $[\alpha]^{26}$D +22.4° (c 0.29, $CHCl_3$); uv max (EtOH) λ (ϵ) 239 nm (10 800); ir ($CHCl_3$) 2.82, 5.71, 5.99, 7.93, 9.01, 9.43, 9.76 μ; NMR ($CDCl_3$) τ 8.95 (3 H, t, J = 7 Hz, CH_2CH_3), 8.80 (3 H, s, 10-CH_3), 8.45 (3 H, s, 13-CH_3), 8.38 (3 H, s, 2′-CH_3), 8.05 (3 H, s, 4-CH_3), 7.92 [3 H, s, C(=O)-CH_3], 7.66 (1 H, dd, J = 14 and 2 Hz, 14-H), 6.82 (1 H, d, J = 7 Hz, 11-OH), 6.43, 5.31 (each 1 H, d, J = 8 Hz, CH_2O), 6.18 (1 H, s, 12-H), 5.83 (1 H, s, 1-H), 5.6 (1 H, br s, OH), 5.35 (1 H, t, J = 3 Hz, 7-H), 5.3 (1 H, m, 11-H), 3.89 (1 H, br s, 3-H), 3.52 (1 H, d, J = 14 Hz, 15-H); mass spectrum m/e 536.2257 (M^+, calcd for $C_{27}H_{36}O_{11}$, 536.2258), 518, 358.1407 (calcd for $C_{20}H_{22}O_6$, 358.1416), 340, 301, 165, 151, 143.0707 (calcd for $C_7H_{11}O_3$, 143.0708), 115, 83.

Anal. Calcd for $C_{27}H_{36}O_{11}$: C, 60.44; H, 6.76. Found: C, 60.54; H, 6.88.

2-Methyl-1,2-butanediol from Quassimarin (1). A suspension of lithium aluminim hydride (7.0 mg, 0.18 mmol) and quassimarin (**1**, 9.7 mg, 0.018 mmol) in ether (1.5 ml) was stirred at room temperature for 4 h. Excess reagent was decomposed with saturated sodium potassium tartrate solution, the precipitate was removed, and the filtrate was concentrated at reduced pressure. Preparative GC afforded 2-methyl-1,2-butanediol which was shown to be identical (NMR, mass spectra, mixture GC analysis) with a sample prepared by conventional methods.[10]

Registry No.—**1**, 59938-97-5; **2**, 35321-80-3.

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(3) The water displaced sap was collected in Costa Rica in the spring of 1974. We thank Dr. M. S. Hudson for supplying the plant material, in accordance with the program developed by the National Cancer Institute.
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A Convenient Preparation of Methyl (*E*)- and (*Z*)-4,4-Dimethoxy-2-butenoates by Electrolyses of Furfuryl Alcohol, Furfural, and 2-Furoic Acid

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Alkyl 4,4-dialkoxy-2-butenoates have been recognized as powerful Michael acceptors in the syntheses of the plant antitumor agent camptothecin[1] and of 11-oxoprostaglandins[2] and also as an unusual Diels–Alder dienophile.[3] Several efforts to obtain 4,4-dialkoxy-2-butenoates by the ozonolysis of 1,3-dienoates and subsequent acetalization, giving the *E* isomer,[3] by the alcoholysis of 4-ethoxy-2-butenolide derived

Table I. Conditions and Results of Anodic Oxidation of 2-Substituted Furans and the Related Compounds

Run	Substrate (g)	Supporting[a] electrolyte	Current, A/cm²	Quantity of electricity, Faradays/mol	Temp, °C	Product yield, % 2a	2b	3a	3b	5
1	**1a** (3.00)	A	0.033	8.0	13–15			75		
2	**4** (1.00)	A	0.083	12.5	27–28			87		
3	**6** (1.00)	B	0.083	12.5	17–23			84		
4	**1b** (1.00)	A	0.033	8.0	15–19		72	24		
5	**1a** (1.00)	A	0.033	2.1	15–16	91				
6	**2a** (1.00)	A	0.066	6.0	19–20			66		
7	**4** (1.00)	A	0.083	2.1	18–20					71
8	**5** (1.00)	A	0.083	10.0	26–27			76		
9	**6** (1.00)	C	0.083	12.5	15–16			3[c]	81	

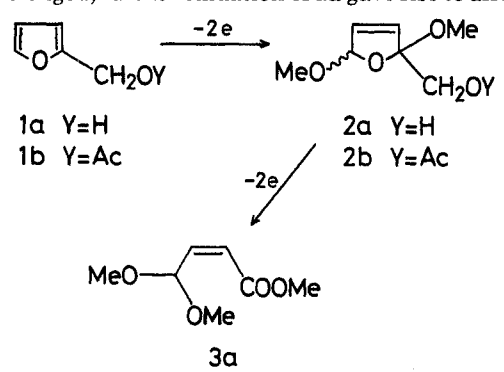
[a] A, Et_4NClO_4 (0.10 g); B, Et_4NClO_4 (0.10 g)–Et_3N (1.00 g); C, NH_4Br (0.10 g)–Et_3N (1.00 g). [b] Isolated yield. Yields are calculated on isolated product based on added starting material. [c] Based on GLC analysis: 10% SE-30 on Chamelite CK 80–100 (3 m × 4 mm) at 145 °C with a flow rate of 20 ml/min.

from photolysis of furfural, giving a mixture of *E* and *Z* isomers,[1,4] and by the Wittig reaction of glyoxal diethyl acetal with ylides, giving *E* isomer,[1a,5] have been recorded. As a consequence of our interest in the method of the electrochemical alkoxylation of 2-substituted furans,[6] we found the highly efficient and selective one-step synthesis of either *Z* or *E* isomer of methyl 4,4-dimethoxy-2-butenoates (**3a** and **3b**) by electrolyses of **1a, 4,** and **6.**

Earlier reports of anodic methoxylation of furan derivatives are those involving the formation of the corresponding 2,5-dimethoxy-2,5-dihydrofurans in sufficient yield.[7] On the other hand, a few examples of converting furfural,[8] 2-furoic acid,[8b] methyl 5-substituted 2-furoates,[9] and methyl 2-thiophencarboxylate[10] into ring opening products, e.g., maleic acid and 4-oxo-2-butenoates, by electrolysis have been reported. However, direct electrosynthesis of alkyl 4,4-dialkoxy-2-butenoates from 2-substituted furans has not yet been realized.

Electrolyses of 2-substituted furans **1a, 1b, 4,** and **6** were carried out under a constant current by using two platinum foil electrodes. The reaction conditions and results are listed in Table I. As shown in runs 1, 2, and 3 (Table I) methyl (*Z*)-4,4-dimethoxy-2-butenoate (**3a**) was obtained by the electrolyses of furfuryl alcohol (**1a**), furfural (**4**), and 2-furoic acid (**6**) in 75–87% yields. In a similar condition, electrolysis of the acetate **1b** afforded the corresponding dihydrofuran **2b** as a major product (72%) along with **3a** (24%).

The coulometric studies of the electrolysis of **1a** revealed that under a current density of 0.02 A/cm² (Figure 1) the extent of formation of **2a** from **1a** appears to be approximately linear with 2.1 Faradays/mol of passed electricity. In this stage most of **1a** was electrolyzed. However, when the electrolysis was prolonged, further oxidation of **2a** gave rise to afford the



2-butenoate **3a** completely after passing a current of 4–6 Faraday/mol. The successful and selective conversion of **1a** into **2a** and/or **3a** could be achieved when the current density was controlled below 0.05 A/cm². If the electrolysis is carried

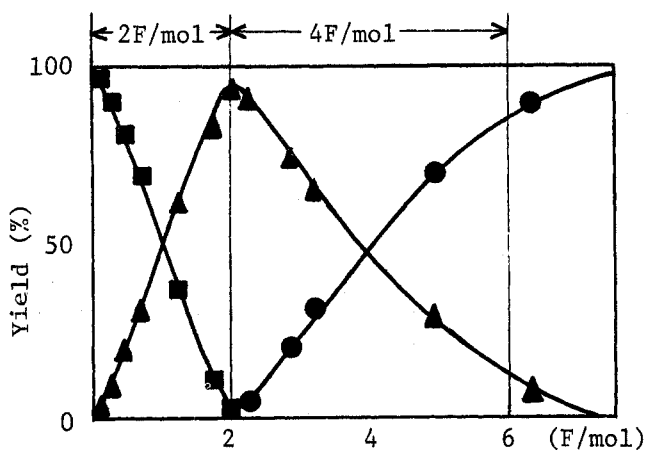
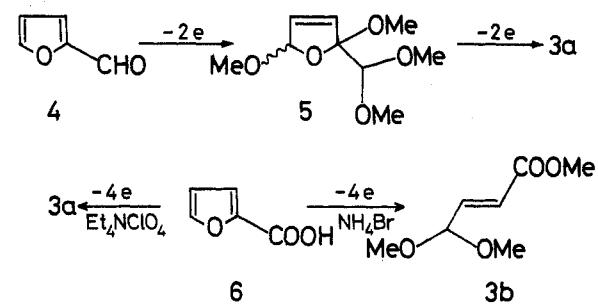


Figure 1. Current density 0.02 A/cm². Experimental points are given for **1a** (■), **2a** (▲), and **3a** (●).

out at a current of 0.2 A/cm², product selectivity is decreased (Figure 2). The conditions and results from stepwise electrolysis of **1a** and/or **2a** are also shown in runs 5 and 6. Electrolysis of furfural (**4**) in methanol under a constant current of 0.083 A/cm² gave 2-dimethoxymethyl-2,5-dimethoxy-2,5-dihydrofuran (**5**) in 71% yield after 2.1 Faradays/mol of current was passed (run 7). The formation of **3a** from **4** via **5**



could be rationalized by the electrolytic conversion of **5** to **3a** as shown in run 8. Electrolysis of the acid **6** using NH_4Br–Et_3N as an electrolyte resulted in *E* isomer **3b** preferably (run 9). The formation of **3b** would be caused by isomerization from **3a** to **3b** by the action of bromine radical,[11] which would be generated by one-electron oxidation of bromide ion on the anode.

A plausible mechanism of the anodic conversion of **2a** to **3a** is depicted in Scheme I. One-electron oxidation of **2a** would be considered to generate an alkoxy radical[12] which undergoes elimination of formaldehyde to give b. Successive one-electron oxidation of b and subsequent nucleophilic attack by meth-

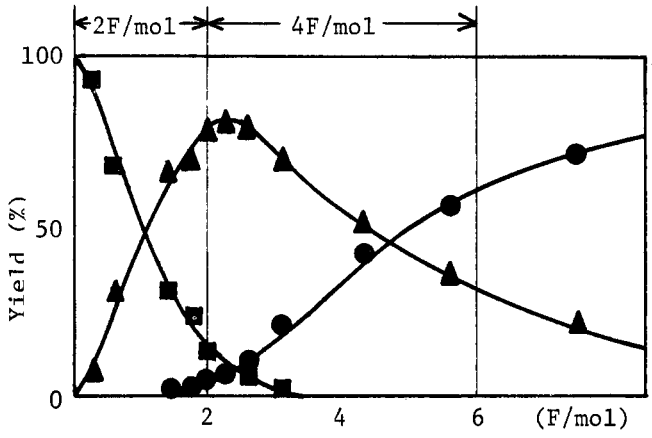
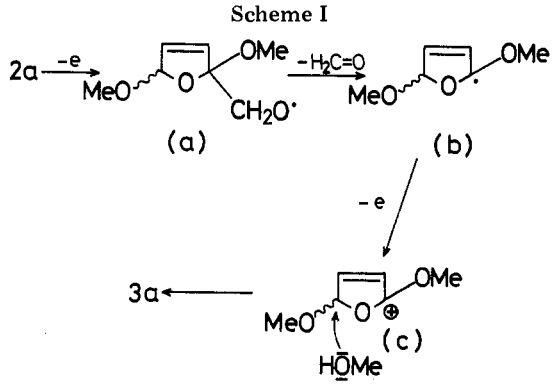


Figure 2. Current density 0.20 A/cm^2. Symbols follow: **1a** (■), **2a** (▲), and **3a** (●).

Scheme I



anol would produce the ring opening product **3a** via the cation intermediate c. In the course of the electrolysis two-electrons oxidation of formaldehyde is also expected to afford methyl formate. After all, the conversion of **2a** to **3a** should require four electrons on the anode. As shown in Figure 1, the conversion of ca. 80% of **2a** was achieved when 4 Faradays/mol of electricity was passed.

Experimental Section

All the boiling points are uncorrected. NMR spectra were recorded on a Hitachi R-24 spectrometer. Ir spectra were measured on neat liquids using a JASCO model IRA-1 spectrometer.

Materials. Commercially available furfuryl alcohol (**1a**) and furfural (**4**) were distilled under reduced pressure before use. 2-Acetoxymethylfuran (**2a**)[13] and 2-furoic acid (**6**)[14] were prepared according to the procedure described in the literature.

General Procedure of the Electrolysis. 2-Substituted furans **1a, 1b, 2a, 4, 5,** and **6** were dissolved in MeOH (20 ml) containing Et_4NClO_4, Et_4NClO_4–Et_3N, and/or NH_4Br–Et_3N as a supporting electrolyte. The solutions were electrolyzed under a constant current in a compartment cell equipped with two platinum foil electrodes (2 × 3 cm^2). The solution was condensed under reduced pressure, taken up in EtOAc, washed with aqueous $NaHCO_3$ and brine, and dried (Na_2SO_4). After evaporation of the solvent the residue was distilled by using a short-path distillation apparatus, to give the products **2a, 2b, 3a, 3b,** and **5.** The detailed reaction conditions and results of electrolyses of 2-substituted furans and the related compounds are listed in Table I. Analytically pure samples were obtained by column chromatography on silica gel with benzene–EtOAc (20/1).

2,5-Dimethoxy-2-hydroxymethyl-2,5-dihydrofuran (2a): bp 82–85 °C (7.5 mm) [lit.[15] bp 106–110 °C (18 mm)]; ir (neat) 3440 (OH), 2820 (CH_3O), 1633 cm^{-1} (C=C); NMR ($CDCl_3$) δ 2.68 (m, 1 H, OH), 3.15–3.72 (8 H, 2 CH_3O, CH_2O), 5.45–6.16 (3 H, CHO, CH=CH).

2-Acetoxymethyl-2,5-dimethoxy-2,5-dihydrofuran (2b): bp 105–109 °C (11 mm) [lit.[15] bp 117–119 °C (12 mm)]; ir (neat) 2820 (CH_3O), 1745 (C=O), 1632 cm^{-1} (C=C); NMR ($CDCl_3$) δ 2.07 (s, 3 H, CH_3CO), 3.15, 3.24 (2 s, 3 H, CH_3O), 3.43, 3.51 (2 s, 3 H, CH_3O), 3.88–4.48 (m, 2 H, CH_2O), 5.45–6.23 (3 H, CHO, CH=CH).

Methyl (*Z*)-4,4-Dimethoxy-2-butenoate (3a): bp 74–78 °C (12 mm); ir (neat) 2820 (CH_3O), 1728 (C=O), 1657 cm^{-1} (C=C); NMR ($CDCl_3$) δ 3.33 (s, 6 H, *gem*-CH_3O), 3.68 (s, 3 H, CH_3O), 5.68 (d, J = 7.2 Hz, 1 H, CH=), 5.87 (s, 1 H, CHO), 5.92 (d, J = 7.2 Hz, CH=).

Anal. Calcd for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.53; H, 7.64.

Methyl (*E*)-4,4-Dimethoxy-2-butenoate (3b):[3,4] bp 75–78 °C (12 mm); ir (neat) 2820 (CH_3O), 1726 (C=O), 1668 cm^{-1} (C=C); NMR ($CDCl_3$) δ 3.33 (s, 6 H, *gem*-CH_3O), 3.77 (s, 3 H, CH_3O), 4.96 (diffused d, J = 4.2 Hz, 1 H, CHO), 6.17 (diffused d, J = 16.2 Hz, 1 H, CH=), 6.76 (dd, J = 4.2, 16.2 Hz, 1 H, CH=).

2,5-Dimethoxy-2-dimethoxymethyl-2,5-dihydrofuran (5): bp 65–70 °C (7 mm) [lit.[15] bp 107–110 °C (13 mm)]; ir (neat) 2824 (CH_3O), 1632 (C=C), 1019, 1027, 978 cm^{-1}; NMR ($CDCl_3$) δ 3.18–3.52 (m, 12 H, CH_3O), 3.75–4.21 (1 H, CHO), 5.50–6.30 (m, 3 H, HC=CH, CHO).

Registry No.—**1a,** 98-00-0; **1b,** 623-17-6; **2a,** 19969-71-2; **2b,** 41991-02-0; **3a,** 57314-31-5; **3b,** 32815-00-2; **4,** 98-01-1; **5,** 59906-91-1; **6,** 88-14-2.

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A Novel Intermolecular Transfer Reaction of Alkenyltrialkylborates with Aqueous Bases and Its Application to the Protonolysis of Alkenylboron Derivatives

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Conversion of organoboranes into organic products is most commonly achieved by either oxidation or protonolysis.[1] Whereas the alkaline hydrogen peroxide oxidation is a highly general reaction,[1] protonolysis with carboxylic acids suffers from a few difficulties, such as the incompatibility with various acid-sensitive functional groups and the frequent need for high temperatures (>100 °C).[2,3] In view of the growing significance of alkenylboron derivatives as synthetic intermediates, development of general and mild procedures for their protonolysis that are complementary to the existing acidic procedure is especially desirable.

We have found that alkenyltrialkylborates (**1**), readily obtainable by the treatment of alkenyldialkylboranes with an alkyllithium reagent, undergo a selective protonolysis reaction