Reaction of Methyl 2-*O*-Benzoyl-3-*O*-methyl-4,6-di-*O*-methylsulfonyl-β-D-mannopyranoside (10) with Potassium Benzoate in Refluxing *N,N*-Dimethylformamide (10 hr). An *N,N*-dimethylformamide solution (10 ml) containing **10** (105 mg, 0.22 mmol) and potassium benzoate (250 mg, 1.56 mmol) was heated at reflux for 10 hr. The precipitate was filtered off and the filtrate was evaporated in vacuo. The residue was chromatographed on silica gel (30 g). Elution with 7:1 benzene–ethyl acetate gave two fractions. The first fraction (23 mg, 20%) was pure **4**, whereas the second fraction (75 mg, 65%) was pure **6**, the **6**:**4** ratio being 3.2:1.

Methyl 3-*O*-Methyl-2-*O*-methylsulfonyl-β-D-galactopyranoside (12). To a methanolic solution (10 ml) of **7** (220 mg, 0.44 mmol), metallic sodium (55 mg, 2.30 mmol) was added and the reaction mixture was heated at 60° for 30 min. The solution was neutralized with acetic acid and the solvents were evaporated in vacuo. The residue was chromatographed on Al_2O_3 (12 g). Elution with benzene (20 ml), ethyl acetate (20 ml), and 1:1 ethyl acetate–methanol (40 ml) gave pure **12** (125 mg, 98%): mp 164–165°; $[\alpha]^{27}D$ +3° (*c* 1.12, CH_3OH); ir ($CHCl_3$) 3500 cm^{-1} (broad peak, OH); NMR ($CDCl_3$) δ 3.37 and 3.28 (two s, 6, C-1 and C-3 methoxy groups), 3.07 (s, 3, methyl from C-2 methylsulfonyl group).

Anal. Calcd for $C_9H_{18}O_8S$: C, 37.76; H, 6.34; S, 11.20. Found: C, 37.82; H, 6.27; S, 10.98.

Methyl 3,4,6-Tri-*O*-methyl-2-*O*-methylsulfonyl-β-D-galactopyranoside (13). To a benzene solution (20 ml) of **12** (117 mg, 0.41 mmol), Ag_2CO_3 (300 mg, 1.1 mmol) and methyl iodide (1 ml, 15.96 mmol) were added and the reaction mixture was heated at reflux for 6 hr. [after 2 hr additional amounts of silver carbonate (300 mg) and methyl iodide (1 ml) were added]. The precipitate was filtered off and the filtrate was evaporated in vacuo. The crystalline residue (132 mg) was chromatographed on silica gel (10 g). Elution with 95:5 benzene–2-propanol gave pure crystalline **13** (119 mg, 92%). An analytical sample was obtained by recrystallization from acetone–isopropyl ether: mp 138°; $[\alpha]^{27}D$ −22° (*c* 0.50, $CHCl_3$); ir ($CHCl_3$) 1360 and 1175 cm^{-1} (asymmetric and symmetric SO_2 stretch); NMR ($CDCl_3$) δ 4.69 (two d, $J_{1,2}$ = 7.8 and $J_{2,3}$ = 9.8 Hz, 1, H-2), 4.31 (d, $J_{1,2}$ = 7.8 Hz, 1, H-1), 3.77 (two d, $J_{3,4} \leq 1$ and $J_{4,5}$ = 3.0 Hz, 1, H-4), 3.56, 3.51 and 3.40 (three s, 12, C-1, C-3, C-4, and C-6 methoxy groups), 3.07 (s, 3, methyl from C-2 methylsulfonyl group).

Anal. Calcd for $C_{11}H_{22}O_8S$: C, 42.03; H, 7.06; S, 10.20. Found: C, 42.36; H, 7.06; S, 9.96.

Reaction of Methyl 3,4,6-Tri-*O*-methyl-2-*O*-methylsulfonyl-β-D-galactopyranoside (13) with Potassium Benzoate in Refluxing *N,N*-Dimethylformamide (120 hr). An *N,N*-dimethylformamide solution (15 ml) containing **13** (81 mg, 0.26 mmol) and potassium benzoate (206 mg, 1.29 mmol) was heated at reflux for 120 hr. The solvent was evaporated in vacuo and the residue (168 mg) was chromatographed on silica gel (15 g). Elution with 95:5 benzene–2-propanol gave the pure crystalline starting material (44 mg, 54%) as the only isolable product.

Registry No.—**1**, 14982-01-5; **2**, 54307-86-7; **3**, 54307-87-8; **4**, 34939-95-2; **5**, 34698-07-2; **6**, 54307-88-9; **7**, 54307-89-0; **8**, 54307-90-3; **9**, 52260-50-1; **10**, 54307-91-4; **11**, 54307-92-5; **12**, 51385-26-3; **13**, 54307-93-6; methanesulfonyl chloride, 124-63-0; potassium benzoate, 582-25-2; benzoyl chloride, 98-88-4.

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Structural Relationships and Interconversions of Isomeric Astilbins[1a]

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Several isomers of astilbin [2(*R*):3(*R*)-3,3′,4′,5,7-pentahydroxyflavanone-3-α-L-rhamnoside] (1) are assigned absolute configurations on the basis of NMR and chiroptical properties. Neoastilbin (2), isoastilbin (3), and neoisoastilbin (4) are assigned 2(*S*):3(*S*), 2(*R*):3(*S*), and 2(*S*):3(*R*) configurations respectively. Similar configurational assignments are made in the engeletin series. Studies of the isomerization of 1 have shown that heating 1 with D_2O–pyridine at 75° results in chalcone formation, while isomerization of 1 in ethanolic NaOAc at room temperature yields selective epimerization at C-2 and C-3.

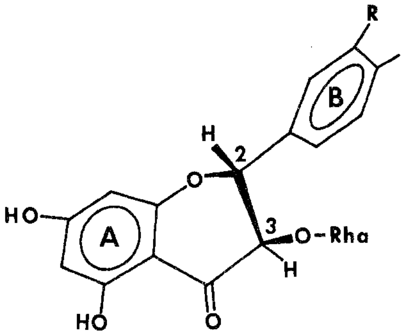
Astilbin (1) and engeletin (5) from wood bark are members of a rare group of natural products,[2] 3-*O*-glycosyl derivatives of 3-hydroxyflavanones. In 1960, Tominaga described isomeric compounds of 1[3] and 5[4] and suggested the existence of cis,trans isomers[5,6] involving C-2 and C-3 of the heterocyclic ring. The preparation of cis-3-substituted flavanones is difficult since acid epimerization readily gives a mixture of cis and trans isomers. cis-3-Hydroxyflavanones are unknown, although *cis*-3-methoxy,[7] *cis*-3-bromo,[8] and *cis*-3-methylflavanones[9] have been prepared[7a,8,9] or isolated.[7b] The structures of the isomeric astilbins and engeletins are established herein and their mecha-

Table I
NMR Spectra[a] of Isomeric Astilbins and Engeletins

Compd	$J_{2,3}$, Hz	H-2	H-3	H-1''[b]	$C_{5''}$-Me[c]
Astilbin (1)	9.5	5.23	4.58	4.15	1.08
Neoastilbin (2)	10.5	5.10	4.64	4.98	0.84
Isoastilbin (3)	2.5	5.50	4.23	4.79	0.86
Neoisoastilbin (4)	2.0	5.43	4.12	4.19	1.01
Engeletin (5)	10.0	5.29	4.66	4.07	1.05
Neoengeletin (6)	10.5	5.17	4.73	5.01	0.81
Isoengeletin (7)	2.5	5.57	4.21	4.79	0.84
Neoisoengeletin (8)	2.0	5.43	4.11	4.19	1.00

[a] Spectra were obtained in DMSO-d_6 at 60°. Chemical shifts are in parts per million from Me_4Si. [b] Anomeric proton of rhamnose. [c] Methyl group on C-5'' of rhamnose.

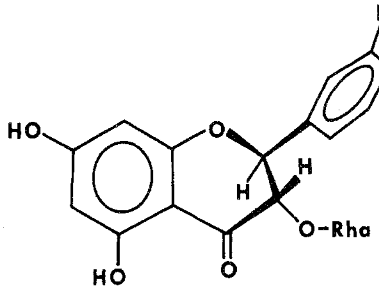
nism of formation under different conditions is discussed. The cis isomers of 1 and 5 represent the first chiral cis-3-substituted flavanones reported.[10]



1 R=OH

5 R=H

Structure of Isomeric Astilbins and Engeletins. Tominaga isolated a trans isomer, neoastilbin (2), and a cis isomer, isoastilbin (3), upon heating 1 in aqueous pyridine. Another cis isomer, neoisoastilbin (4), was isolated upon treating 1 with ethanolic sodium acetate. The cis,trans assignments of 2, 3, and 4 were based[5] upon dehydrogenation of the four isomers to quercitrin and by acidic hydrolysis of the isomers to L-rhamnose and either (+)- or (−)-*trans*-dihydroquercetin in addition to red-shifted uv spectra shown by two of the isomers.



2 R=OH

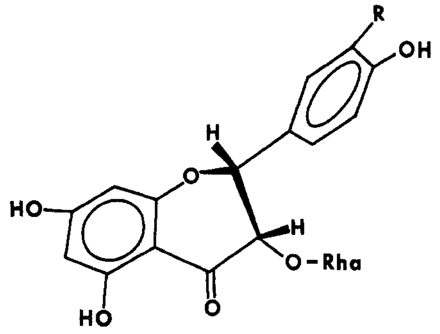
6 R=H

Examination of the NMR spectra (Table I) showed that 1 and 2 possess trans configurations, since they show coupling constants $J_{2,3}$ of 9.5 and 10.5 Hz, respectively; cis configurations are assigned to 3 and 4 which show coupling constants $J_{2,3}$ of 2.5 and 2.0 Hz, respectively.

Table II
CD Spectra[a] of Isomeric Astilbins and Engeletins

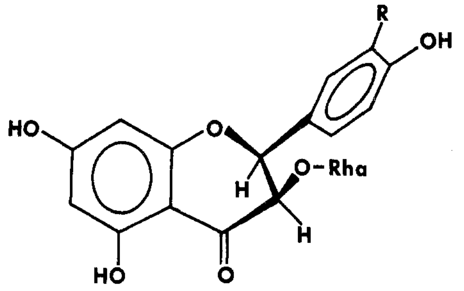
Compd	n → π*	π → π*
Astilbin (1)	$[\theta]_{329}$ +14,000	$[\theta]_{294}$ −31,800
Neoastilbin (2)	$[\theta]_{331}$ −13,400	$[\theta]_{295}$ +31,200
Isoastilbin[b] (3)	$[\theta]_{343}$ +15,200	$[\theta]_{296}$ −37,700
Neoisoastilbin (4)	$[\theta]_{342}$ −18,900	$[\theta]_{296}$ +49,000
Engeletin (5)	$[\theta]_{327}$ +15,500	$[\theta]_{292}$ −42,300
Neoengeletin (6)	$[\theta]_{328}$ −12,600	$[\theta]_{292}$ +31,200
Isoengeletin (7)	$[\theta]_{343}$ +17,500	$[\theta]_{299}$ −36,300
Neoisoengeletin (8)	$[\theta]_{341}$ −16,100	$[\theta]_{296}$ +45,400

[a] All measurements were obtained in methanol. [b] Contaminated with 25–30% astilbin.



3 R=OH

7 R=H



4 R=OH

8 R=H

Compound 1, of known 2(*R*):3(*R*) configuration,[2,11] shows a positive Cotton effect near 330 nm and 2, obviously of 2(*S*):3(*S*) configuration, has a negative n → π* CD band (Table II). Since CD measurements of 3-hydroxyflavanones and their glycosides are known[12,13] to reflect the ring chirality of the sofa conformation of the heterocyclic ring, the chiroptical data of trans isomers 1 and 2 may serve as standards. The positive CD of 3 and negative CD of 4 establish the ring chiralities of these two cis isomers as shown. The question remaining concerns which of the two bulky groups in the cis compounds is axial and which equatorial.[14] Inspection of molecular models show severe steric crowding if the 2-aryl group is axially oriented. Furthermore, the 3-rhamnosyl group is able to adopt a more sterically favorable quasi-axial position owing to the neighboring sp^2 carbonyl group. In addition, CD spectra favor axial orientation for the 3-rhamnosyl group in 3 and 4 since the Cotton effects are red shifted by 12–13 nm in comparison to 1 and 2. α-Axial substitution by an electronegative group often red shifts the uv maximum and corresponding CD band of car-

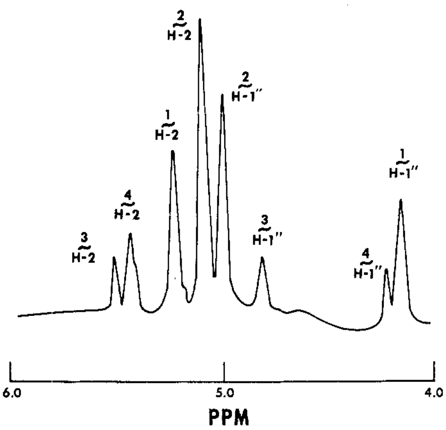
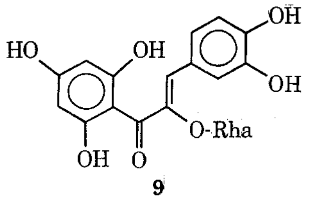


Figure 1. Partial NMR spectrum (100 MHz) of isomers resulting from treatment of 1 with D_2O–pyridine at 75°. The spectra in this and subsequent figures were obtained in DMSO-d_6 at 60°.

bonyl n → π* transitions.[15] Therefore, 3 and 4 can be assigned 2(*R*):3(*S*) and 2(S):3(*R*) configurations,[16] respectively. Similarly **5**, neoengeletin (**6**), isoengeletin (**7**), and neoisoengeletin[17] (**8**) are 2(*R*):3(*R*), 2(S):3(S), 2(R):3(S),[18] and 2(S):3(R),[18] respectively.

Since trans isomers **1** and **2** and cis isomers **3** and **4** are diastereomers and not enantiomers, they should possess slightly different preferred conformations in solution. Subtle differences are observed in the CD curves, since neither **1** and **2** nor **3** and **4** possess exact mirror image curves. More impressive evidence is seen by NMR, where the anomeric proton is deshielded 0.6–0.8 ppm in **2** and **3** relative to **1** and **4**. Also, the *C*-methyl protons in **2** and **3** are shielded ~0.2 ppm relative to the same resonances in **1** and **4**. These NMR shifts reflect interactions between the rhamnose and B ring. Apparently, *cis*-**3** and *trans*-**2** have similar preferred solution conformations in which the rhamnose has the $C_{5''}$-methyl located above the center of the B ring in the shielding cone and the H-1'' near the circumference of the B ring in a deshielding region. On the other hand, this conformation(s) is not as prominent in *cis*-**4** and *trans*-**1**.



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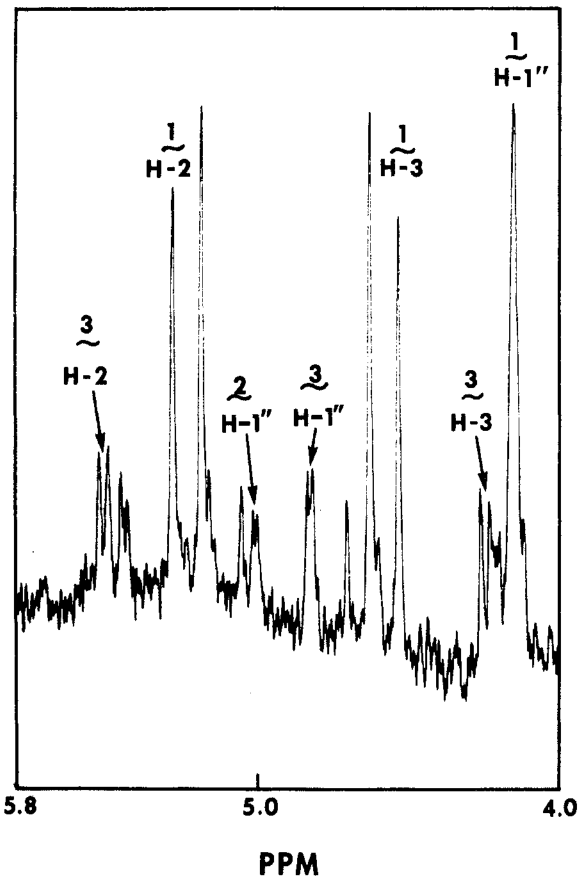
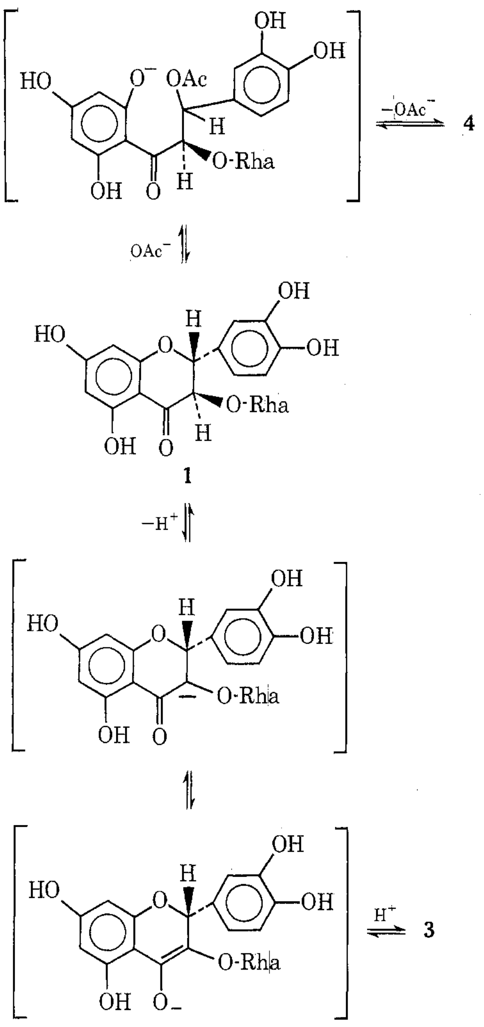


Figure 2. Partial NMR spectrum (100 MHz) of isomers resulting from treatment of 1 with aqueous ethanolic NaOAc at room temperature.

Interconversion of Isomeric Astilbins.[19] The isomerization of compounds **1**, **2**, **3**, and **4** was studied via NMR spectroscopy of a mixture of the four isomers. Heating astilbin at 75° in D_2O–pyridine for several hours produced all four isomers and incorporated deuterium at C-3 in each one. Under protonating conditions the C-2 protons appear as doublets, since they are coupled to the C-3 protons located at higher field, but in D_2O–pyridine the C-2 resonances collapsed to singlets (Figure 1). Only eight singlets remained in the spectrum of the deuterated products between 4.0 and 5.7 ppm, the four at lower field due to C-2 resonances and the four upfield due to anomeric protons of **1**, **2**, **3**, and **4**. These results implicate a chalcone (**9**) as an intermediate,[20] since all four isomers could arise from such an intermediate. The proton at C-3 would be expelled upon formation of **9**, being replaced upon recyclization by deuterium. Isomerization of astilbin in aqueous pyridine at 75° probably produces an equilibrium mixture of isomers, since **9** should allow product distribution as a function of thermodynamic stability. Trans isomers **1** and **2** comprised 68% of the reaction product and cis isomers **3** and **4** 32%, a ratio very similar to the equilibrium ratio of trans to cis isomers found[21] for a substituted 3-methoxyflavanone. Molecular models indicate that either a methoxy or rhamnosyl group can be accommodated equally well in a quasi-axial 3 position of a 3-hydroxyflavanone. The fact that **2** predominated over **1** in the trans series and that **3** occurred in greater amounts than **4** in the cis pair is consistent with the observation of interactions between the rhamnose and B ring in **2** and **3** (vide supra). These interactions could stabilize **2** and **3** and result in their preferential formation under equilibrium conditions such as the aqueous pyridine isomerization at 75°.

On the other hand, treatment of **1** with ethanolic sodium acetate at room temperature leads to different results. Examination of the NMR spectrum (Figure 2) of the reaction products under protonating conditions in ethanolic sodium acetate shows the presence of all four isomers, although **2** consists of only 7–13% of the reaction product. Since this trans isomer is the most stable of the four isomers (vide supra), its presence in such small amounts rules out the chalcone intermediate. The major reaction products are cis isomers **3** and **4**, each in 15–20% yield. The reaction product contains 55% astilbin, most of which is unreacted starting material. One notable change was observed in the NMR spectrum (Figure 3) of the reaction products obtained in D_2O–ethanol-*O*-d_1–NaOAc. The C-3 proton of **3** has been largely replaced by deuterium, thus causing the collapse of the C-2 proton resonance to a singlet. These results suggest that the cis isomers are formed by selective epimerization of **1**. A possible pathway is outlined in Scheme I. The C-2 epimer, **4**, could be formed by ring opening without chal-

Scheme I



cone formation and then ring closure giving both 1 and 4. This reaction could readily occur in the presence of acetate, since C-2 should possess considerable carbonium ion character. The C-3 epimer, 3, could result from proton removal at C-3 with formation of a carbanion or enolate anion followed by proton return to yield 3 or 1. The small amount of 2 formed could result from either mechanism operating on cis isomers 3 and 4. Apparently the isomerization of 1 in ethanolic sodium acetate at room temperature proceeds under kinetic control. Isomerization of 1 in D_2O–pyridine at room temperature gave results similar to the ambient studies in ethanolic sodium acetate. After standing for 24 hr only cis isomers 3 and 4 had been produced while longer reaction times eventually led to predominant formation of 2.

Finally, isomerization of 1 in refluxing D_2O solution gave an isomeric mixture in which all isomers possessed deuterium at C-3. However, the isomeric ratio was quite different from the aqueous pyridine isomerization at 75°, since some of the astilbin was obviously unreacted. Probably the chalcone intermediate is primarily responsible for the isomerization resulting from refluxing 1 in water for 48 hr.

Experimental Section[22]

Materials. The data in Tables I and II were obtained on isomeric astilbin and engeletin samples provided by Tominaga (cf. ref 3–6). Astilbin used for isomerization studies (Figures 1–3) was obtained by ethanol extraction of *Quintinnia serrata* bark.[23] Ethanol-O-d_1 was prepared according to Streitwieser et al.[24] and was 99.3% deuterated by NMR measurements. THF was distilled twice, first from CaH_2, then from $NaAlH_2(OCH_2CH_2OCH_3)_2$, and estimated to contain 0.2% water by ir measurements. Sodium acetate was fused in a low-humidity room and found to contain 0.15% HDO by NMR measurement against a known amount of D_2O in dioxane. The labile protons in astilbin samples used for isomerization studies were exchanged by treatment with D_2O.

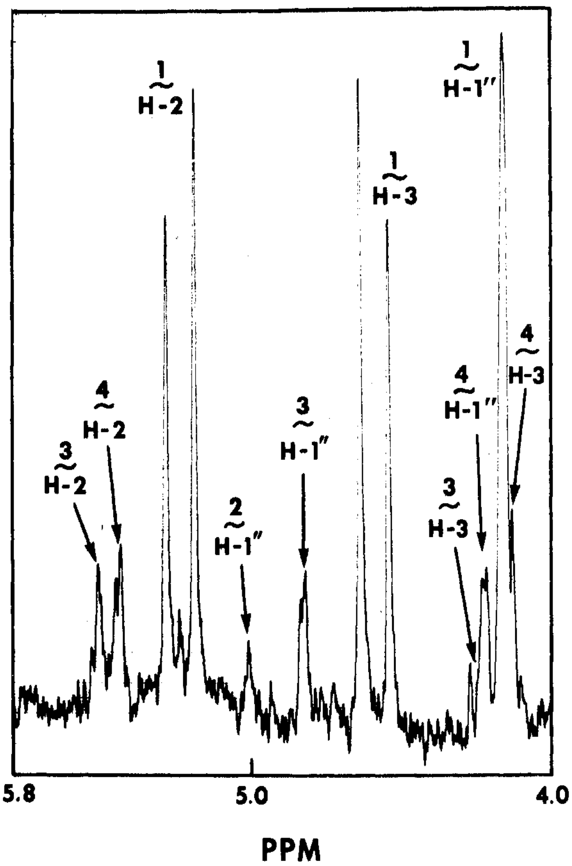


Figure 3. Partial NMR spectrum (100 MHz) of isomers resulting from treatment of 1 with D_2O–ethanol-O-d_1–NaOAc at room temperature.

Isomerization Studies. A. Pyridine–D_2O. Astilbin (0.20 g) was dissolved in dry pyridine (4 ml) and D_2O (36 ml) and heated for 3.5 hr at 75° under nitrogen. The apparent pH of the reaction mixture was 7.3. After solvent removal in vacuo at 0.05 Torr (room temperature) and drying over P_2O_5 at 100° (0.2 Torr), 0.18 g of isomeric product was obtained containing 24% 1, 46% 2, 16%, 3, and 14% 4 (see Figure 1).

A similar run under protonating conditions gave a mixture containing 22% 1, 46% 2, 19% 3, and 13% 4.

B. Ethanolic Sodium Acetate. Astilbin (0.20 g) and NaOAc (0.50 g) were dissolved in ethanol-O-d_1 (50 ml) and D_2O (20 ml). After standing in a drybox for 48 hr with occasional shaking, the reaction mixture was taken to dryness in vacuo (0.05 Torr) at room temperature. Three portions (10 ml) of carefully dried THF were used to extract the isomeric astilbins from the NaOAc. After solvent removal and drying, 0.12 g of product was obtained consisting of 49% 1, 7% 2, 24% 3, and 20% 4.

A similar run under protonating conditions gave 47% 1, 13% 2, 23% 3, and 17% 4.

C. D_2O. Astilbin (0.15 g) was dissolved in D_2O (99.8%) and refluxed for 48 hr under nitrogen. The apparent pH of the reaction mixture was 4.1. After work-up as in A, a reaction product (0.12 g) consisting of 40% 1, 26% 2, 14% 3, and 20% 4 was obtained. The A-ring protons were completely exchanged under these conditions.[25]

A similar run under protonating conditions gave 51% 1, 17% 2, 10% 3, and 22% 4.

Registry No.—1, 29838-67-3; 2, 54081-47-9; 3, 54081-48-0; 4, 54141-72-9; 5, 572-31-6; 6, 54081-49-1; 7, 30987-58-7; 8, 54081-50-4.

References and Notes

(1) (a) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971; see Abstracts, CELL-65. (b) Agricultural Research Service, U.S. Department of

Agriculture.

(2) Cf. K. R. Markham and T. J. Mabry, *Tetrahedron,* **24,** 823 (1968), for other examples.

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(14) While 2,3-diaxial substituents have been observed[9] in some 4-oximinoflavans, no 2-axial aryl substituents have been found in either flavanones or 3-substituted flavanones and such a possibility seems extremely remote in the case of **3** and **4** according to the precepts of conformational analysis.

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(16) These configurations are opposite to those originally proposed in ref 5.

(17) The existence of stable rhamnosides of *cis*-3-hydroxyflavanones suggests that mild hydrolytic conditions, such as enzymatic, might yield the presently unknown *cis*-3-hydroxyflavanones. However, our cursory attempts to hydrolyze neoisoengeletin with fungal hemicellulase were unsuccessful.

(18) These configurations are opposite to those originally proposed in ref 6.

(19) We have studied the isomerization of **1** in aqueous pyridine at 75° and in ethanolic sodium acetate at room temperature for the reason that the original preparation[3] of **2, 3,** and **4** was conducted under similar conditions.

(20) Cf. T. Tominaga, *J. Pharm. Soc. Jpn.,* **80,** 1212 (1960), for previous mechanistic discussions of the astilbin isomerization.

(21) J. W. Clark-Lewis and V. Nair, *Tetrahedron Lett.,* 5467 (1966).

(22) NMR spectra were measured on a Varian HA-100 spectrometer with tetramethylsilane (Me_4Si) as the internal standard. CD spectra were obtained with the aid of a Cary 6003 dichrometer.

(23) Cf. R. C. Cambie, *J. Chem. Soc.,* 848 (1959). The authors thank Professor Cambie for a generous sample of the bark.

(24) A. Streitwieser, L. Verbit, and P. Stang, *J. Org. Chem.,* **29,** 3706 (1964).

(25) Cf. E. S. Hand and R. M. Horowitz, *J. Am. Chem. Soc.,* **86,** 2084 (1964).

A Simple Method for Determining the Configurations of Tertiary Alcoholic Centers in Branched-Chain Carbohydrate Derivatives by Use of Europium(III)-Induced Shifts in the ^{1}H Nuclear Magnetic Resonance Spectrum[1-3]

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The addition of graduated amounts of a solution of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III) [$Eu(fod)_3$] to solutions of the sugar derivatives methyl 3,4-*O*-isopropylidene-2-*C*-(2-methyl-1,3-dithian-2-yl)-β-D-ribopyranoside (**1**), methyl 2-*C*-(1,3-dithian-2-yl)-3,4-*O*-isopropylidene-β-D-ribopyranoside (**2**), 4,6-dideoxy-1,2-*O*-isopropylidene-3-*C*-(2-methyl-1,3-dithian-2-yl)-α-D-*ribo*-hexopyranose (**3**), 4,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexopyranose (**4**), methyl 6-deoxy-2,3-*O*-isopropylidene-4-*C*-(2-methyl-1,3-dithian-2-yl)-α-L-talopyranoside (**5**), methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (**6**), 3-*C*-(1,3-dithian-2-yl)-1,2:4,5-di-*O*-isopropylidene-β-D-psicopyranose (**7**), and 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**8**) produces displacements of the resonance frequencies of protons in approximate proportion to the amount of $Eu(fod)_3$ added. Comparison of the magnitudes of this proportionality (shift gradient) for each identifiable proton resonance of a tertiary alcoholic derivative (**1, 3, 5,** or **7**) with that of the corresponding proton resonance of an alcohol of known stereochemistry (**2, 4, 6,** or **8,** respectively) is used to relate the configuration of the tertiary alcoholic center at the chain-branched position to that of the reference compound; uniform correspondence of the entire set of shift gradients is taken as evidence that the same relative configuration prevails in both the chain-branched tertiary alcohol and the reference molecule, whereas any gross deviation from parallelism in magnitude of corresponding shift-gradient terms in the two sets of values indicates that the tertiary alcoholic center is epimeric to the corresponding center in the reference alcohol. Statistical analysis of these shift-gradient data further supports the configurational assignments.

Configurational assignment of secondary alcoholic centers in carbohydrate molecules is often accomplished, after appropriate derivatization, by analysis of spin-coupling interactions observed in the NMR signal of the secondary CH proton.[4] Analogous molecules having tertiary alcoholic centers, which are accessible by the addition of carbon nucleophiles to a free carbonyl group in glycosulose derivatives,[5] have no proton at the newly formed asymmetric center and thus cannot be examined by the direct ^{1}H NMR technique. The stereochemistry at C-2 of methyl 2-*C*-formyl-β-L-arabinopyranoside was identifiable[5] because the formyl group forms an internal hemiacetal with the 4-hydroxyl group. Continued efforts in the same laboratory revealed that the change in electrophoretic mobility caused by complexation with benzeneboronic acid is configurationally determined and that the intramolecularly hydrogen-bonded O–H stretching frequency in the infrared spectrum is dependent upon the axial or equatorial disposition of the hydroxyl group involved; both of these observations can be applied to configurational elucidation[6] of a somewhat broader, but still limited range of examples.

Synthetic programs in our two laboratories have applied nucleophilic addition to free carbonyl groups in protected sugar derivatives as a general means of extending[7-9] or branching[9-12] the carbon chain of sugar molecules. The utility of these addends as potential intermediates in synthetic schemes has occasioned a renewal in our laboratories of the quest for convenient, general methods of assigning the relative configuration of the tertiary alcoholic center of molecules such as those formed in the quaternization reaction of glycosulose precursors.

^{13}C NMR spectroscopy has been employed successfully