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Synthesis of Dihydro Diols and Diol Epoxides of Benzo[*f*]quinoline

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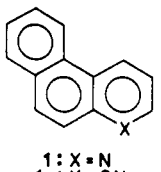
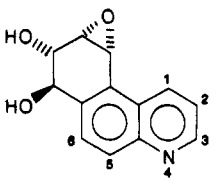
The syntheses of two non-K-region trans dihydro diols **21** and **30** and three diol epoxides **23**, **26**, and **36** of benzo[*f*]quinoline (**1**) are described. The dihydro diols **21** and **30** were obtained from 7,8,9,10-tetrahydrobenzo[*f*]quinoline (**3**) via the *trans*-7,8-diacetoxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (**14**) and its trans 9,10-diacetoxy isomer (**15**) by benzylic bromination followed by dehydrobromination. The trans tetrahydro diacetates **14** and **15** were obtained through the alkenes **6** and **7** and their epoxide derivatives **10** and **11**. The oxidation of dihydro diol **21** with *m*-CPBA failed to produce anti diol epoxide **2**. The presence of *N*-oxides **22** and **23** in the reaction mixture indicated that the oxidation preferentially occurred at nitrogen of **21**. On the other hand, cis diol epoxide **26** was obtained by treatment of diacetate **26** with NBA followed by cyclization with Amberlite resin and hydrolysis of the resulting diacetoxy epoxide **25**. Reaction of **29a** with NBA produced a mixture of two stereoisomeric bromohydrins **32** and **33** which did not cyclize with Amberlite resin. Therefore, tetra-*n*-butylammonium hydrogen sulfate was employed as ring closing agent. ^{1}H NMR, UV, and mass spectra of benzo[*f*]quinoline derivatives are reported.

Benzo[*f*]quinoline (**1**) is an environmental contaminant which has been detected in automobile exhaust, urban air particulates, and cigarette smoke.[2-5] It has been shown to be carcinogenic in rats and mice[6] and also metabolically activated to produce mutagenic products.[7-9] In contrast to **1**, its carbon analogue phenanthrene (**1a**) is neither



1: X = N
1a: X = CN



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mutagenic nor carcinogenic.[10] Since benzo[*f*]quinoline requires metabolic activation for expressing its mutagenic activity, one of the mechanisms by which the aza substitution may modify the mutagenicity/carcinogenicity of phananthrene is through its influence on the reactions involved in the metabolism of this chemical.

LaVoie et al.[11] demonstrated that the incubation of **1** with rat liver homogenates afforded several metabolites, some of which were tentatively identified as 7,8-dihydrobenzo[*f*]quinoline-7,8-diol (**21**), 9,10-dihydrobenzo[*f*]-quinolinediol (**30**), *N*-oxide, and -7-ol on the basis of their UV absorption spectrum and/or ^{1}H NMR spectrum. There is now sufficient evidence to indicate that many carcinogenic polycyclic aromatic hydrocarbons[12] and their aza analogues[13-16] undergo enzymatic activation to bay region diol epoxide derivatives analogous to **2**, which then react covalently with DNA and RNA to produce muta-

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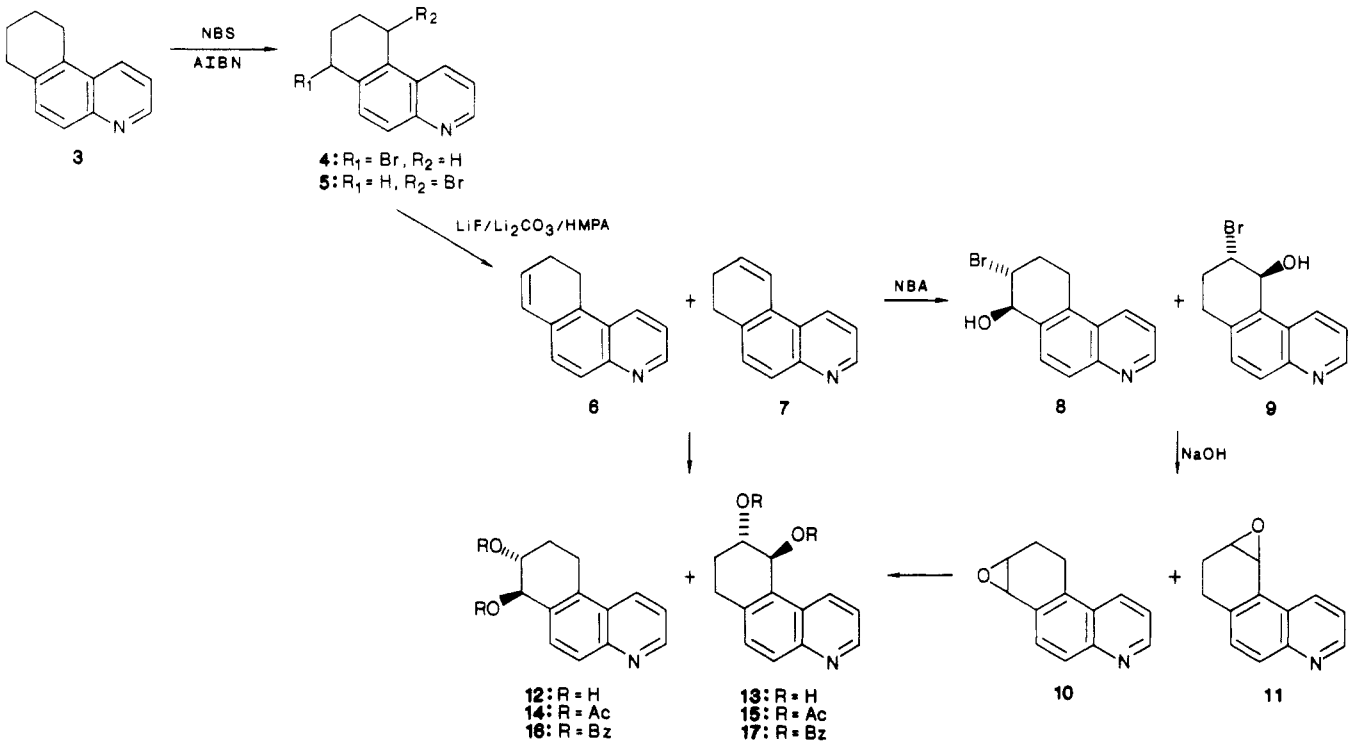
Scheme I



genic/carcinogenic effects. It is, therefore, possible to speculate that **2** is the ultimate carcinogen/mutagen of **1**. In order to test this hypothesis and to assess the role of the aza substituent in the metabolism and in the carcinogenicity and mutagenicity of **1**, various dihydrodiol and diol epoxide derivatives of benzo[*f*]quinoline are required. The present paper describes the synthesis of dihydrodiols **21** and **30** and their epoxides **23**, **26**, and **36**.

Results and Discussion

Synthesis of Dihydro Diols. The corresponding tetrahydro benzo derivatives of azapolycyclic aromatic hydrocarbons (aza-PAHs) seem to be the most appropriate starting point for preparing various non-K-region dihydro diols of different aza-PAHs.[17-19] Accordingly, 7,8,9,10-tetrahydrobenzo[*f*]quinoline (**3**) was selected as the synthetic intermediate for our present work and was obtained in large quantity according to the literature procedure.[20]

Radical bromination of **3** with *N*-bromosuccinimide (NBS) in the presence of α,α'-azobis(isobutyronitrile) (AIBN) afforded (60–70% conversion) a mixture of two regioisomers **4** and **5**, which were subsequently dehydrobrominated with LiF and Li_2CO_3 in hexamethylphosphoramide (HMPA) to produce a mixture of two isomeric alkenes (**6** and **7**). The signals at δ 6.55 (H_7) and 7.15 (H_{10}) in the ^1H NMR spectrum of the mixture indicated **6** and **7** to be present in the ratio of 2:3 along with **3** and **1**. Due to the similar chromatographic properties of the isomeric alkenes **6** and **7**, no attempt was made to separate them. The mixture of alkenes **6** and **7** was converted to trans tetrahydro diols **12** and **13** in 13.2% yield (based on **3**) via the Prevost reaction with silver benzoate and iodine in refluxing benzene followed by alkaline hydrolysis of the resulting mixture of trans dibenzoates **16** and **17**. An alternative route via bromohydrin proved more effective for the preparation of a mixture of tetrahydro diols **12** and **13**. In this preferred route, the mixture of **6** and **7** was treated with *N*-bromoacetamide (NBA) in the presence of HCl to obtain a mixture of tetrahydro bromo hydrins **8** and **9**. A small amount of this mixture was separated by preparative TLC (silica gel) to produce pure forms of **8** and **9**. However, due to the similar chromatographic properties, the separation of bromo hydrins by column chromatography in gram quantities was unsuccessful. Thus, for large scale synthesis, the mixture of bromo hydrins **8** and **9** was treated with alkali to produce a mixture of two regioisomeric tetrahydro epoxides **10** and **11**, which on treatment with formic acid produced a mixture of trans tetrahydro diols **12** and **13** (32.6% yield based on **3**). The resulting mixture of trans tetrahydro diols was acetylated with Ac_2O/pyridine to afford a mixture of trans diacetates **14** and **15**. Separation of **14** and **15** was readily achieved by chromatography on dry column grade silica gel. In this manner, **3** could be converted in six steps into **14** and **15** in overall yields of 9% and 6.6%, respectively, without an extensive purification of intermediates (see Scheme I).

Bromination of the trans diacetates **14** and **15** was effected with NBS. A mixture of bromo diacetates **18** and **19**, obtained from **14**, was readily purified by the addition of ether which precipitates the major isomer **18**. A close similarity in the ^1H NMR spectrum of **18** and that of the corresponding derivative of phenanthrene[17] permitted the assignments of the stereochemistry of **18**, where the benzylic acetate and bromine atom are cis. In a similar manner, **15** produced a mixture of bromo diacetate **28** along with a minor amount of dibromo diacetate **27**. These two compounds were separable on preparative TLC (silica gel). The ^1H NMR data were inadequate to permit an unambiguous assignment of the stereochemistry of **28** (Scheme II).

The bromo diacetate **18** was dehydrobrominated either with LiF and Li_2CO_3 in HMPA or with 1,5-diazabicyclo-

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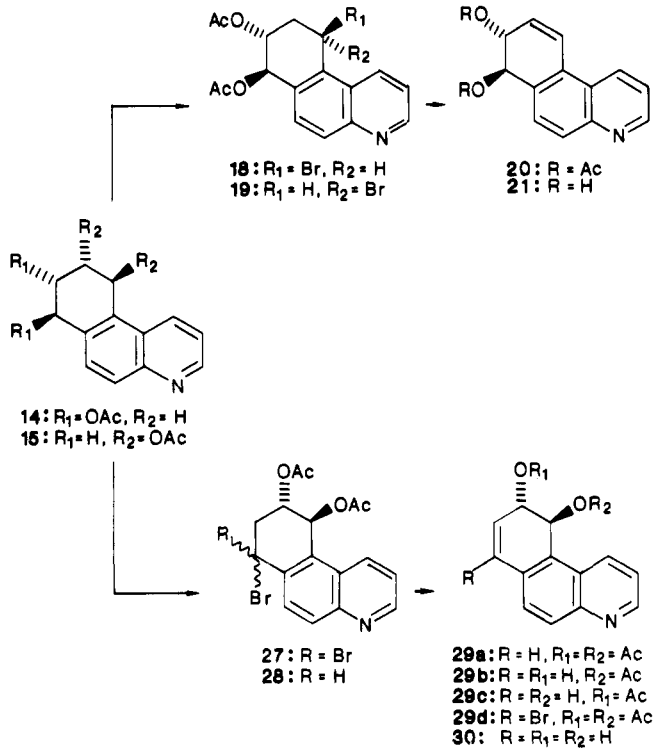
Scheme II



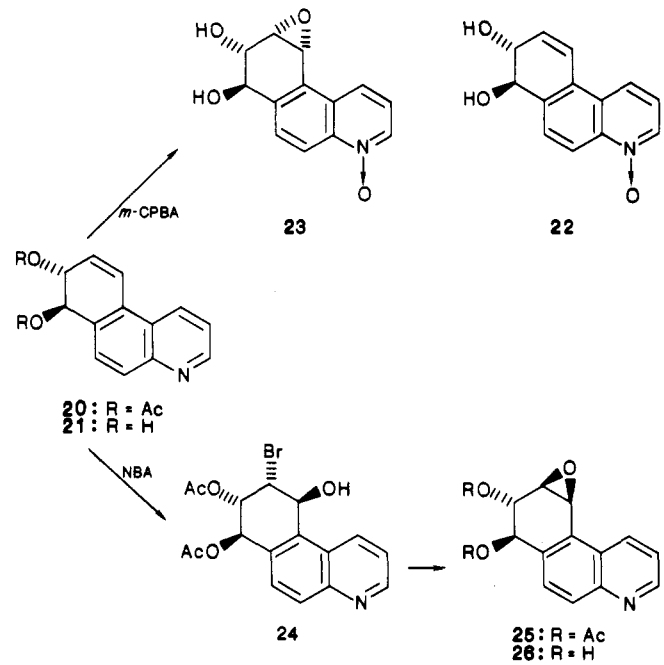
[4.3.0]non-5-ene (DBN) in THF to trans dihydro diacetate **20** in high yields. The stereoisomeric mixture of **18** and **19** also produced a high yield of **20** under these conditions. Although the bromo diacetate **28** was dehydrobrominated exclusively to **29a** in the presence of LiF and Li_2CO_3 in hexamethylphosphoramide (HMPA), the treatment of **28** with DBN in THF produced partially deacetylated products **29b** and **29c** along with **29a**. The replacement of **28** with a mixture of **27** and **28** in the dehydrobromination reaction (LiF and Li_2CO_3 in HMPA) produced a mixture of **29a** and **29d** which was readily separated by preparative TLC. The hydrolysis of the trans diacetates **20** and **29a** with NaOH in THF/MeOH produced the corresponding dihydro diols **21** and **30** in moderate yields (Scheme II).

The ^1H NMR and UV spectra (see Experimental Section) of the dihydro diols **21** and **30** were identical with those tentatively identified by LaVoie et al.[11] in their studies on the metabolism of benzo[f]quinoline by rat liver homogenate.

Synthesis of Tetrahydro Diol Epoxides. The usual procedure described in the literature, for synthesizing an anti diol epoxide (epoxide in the bay region) such as **23**, involves the treatment of the dihydro diol with *m*-chloroperoxybenzoic acid while the treatment of the dihydro diol with NBA followed by cyclization gives the syn diol epoxide such as **26**.

Because of a poor yield and low solubility of the dihydro diol **21**, the use of trans diacetate **20** as a possible starting material for the synthesis of **2** was investigated. The reaction of **20** with *m*-chloroperoxybenzoic acid in CH_2Cl_2 or THF produced a mixture of products which were difficult to identify. Therefore, **21** was treated with an excess of *m*-chloroperoxybenzoic acid in excess of dry THF at room temperature for 24 h to obtain exclusively **23**, *N*-oxide of **2**. The *N*-oxide structure of the product was deduced from its mass spectrum (M^+, *m/e* 245) and the ^1H NMR data (see Experimental Section), i.e., the upfield resonance of the H_1 and H_3 as compared with the dihydro diol **21** and diol epoxide **26**. When the above reaction was carried out only for 4 h, an additional product (**22**) was

Scheme III

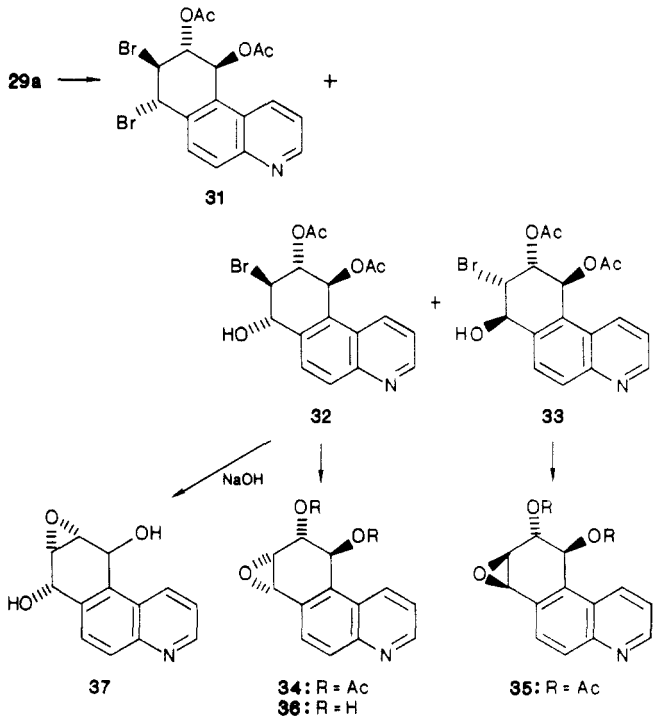


present in minor amounts in the reaction mixture as indicated by TLC (silica gel, 10% MeOH in $CHCl_3$). Because of an extremely low solubility in appropriate solvents, the separation of **22** and **23** could not be achieved. The presence of **22** in the mixture was deduced from the ^1H NMR data of the mixture. On the basis of the chemical shifts of carbinol and olefinic protons (H_7–H_{10}), the compound **22** appeared to be similar to dihydro diol **21**. However, a difference in the NMR signals of the aromatic protons, especially the resonance of H_3 at higher field as compared to the chemical shift of H_3 in **21** ($\Delta\delta$ = 0.4 ppm) clearly indicates that **22** is the *N*-oxide of **21** (Scheme III).

Treatment of **20** with NBA produced the bromo hydrin **24** in good yield. The presence of cis configuration between H_8 and H_9 is shown in the ^1H NMR spectrum of **24** by the small coupling constant ($J_{8,9}$ = 2.8). A large coupling constant must be observed in order to have a trans configuration between H_8 and H_9 (e.g., **32**, $J_{8,9}$ = 10.22). Treatment of **24** with Amberlite-400 (OH-form) produced the diacetate epoxide **25** which on saponification at 0 °C produced diastereomeric diol epoxide **26**. **26** was also obtained by a similar saponification of **24** in one step (Scheme III).

In a similar manner, the trans diacetate **29a** was converted to the diol epoxide **36** (Scheme IV). Thus, the treatment of **29a** with NBA in the presence of HCl yielded a mixture of three compounds **31**, **32**, and **33**. **31** was isolated by an addition of ether into the crude product. The repeated recrystallization of a mixture of **32** and **33** (6:1) produced pure **32** with considerable loss; however, **33** could not be obtained in a pure form. The bromine content of **31** (found, 32.66%; calcd 35%) indicated that it was mostly a dibromide derivative of **21a**. The stereo-chemistry of **31**, **32**, and **33** could easily be assigned on the basis of the coupling constants in their ^1H NMR spectra. Thus, the coupling constants of the major isomer **32** ($J_{7,8}$ = 9.56, $J_{8,9}$ = 10.2, and $J_{9,10}$ = 4.6) clearly suggest that this compound predominantly exists in boat conformation and H_8 and H_9 are trans to each other. On the other hand, coupling constants for the minor isomer **33** ($J_{7,8}$ = 8.9, $J_{8,9}$ = 2.3, and $J_{9,10}$ = 3.3) demonstrate that **33** prefers the half-chair form and H_8 and H_9 are cis to each other. The stereochemistry of **32** is further established from the fact

Scheme IV



that **32** is mostly cyclized to epoxide **37** in the presence of sodium hydroxide, as determined by the ^{1}H NMR spectrum of the crude reaction product (as diacetate). Since the compound **31** has the coupling constants ($J_{7,8}$ = 10.0, $J_{8,9}$ = 9.55, and $J_{9,10}$ = 5.6) similar to those exhibited by compound **32**, its relative stereochemistry was assigned similar to that of **32**. Due to a lack of pure **32** in sufficient quantity, the mixture of **32** and **33** (6:1) was used to prepare the corresponding diacetate epoxides **34** and **35**. Since the cyclization of **32** and **33** failed to occur in the presence of Amberlite resin-400 (OH-form), phase-transfer catalyst (n-$Bu_4N^+HSO_4^-$) was employed (see Scheme IV) to achieve cyclization of **32** and **33** without any significant deacetylation. The crude mixture of **34** and **35**, thus obtained, was purified by repeated recrystallizations to produce pure **34**. Compound **35** could not be obtained in a pure form. Finally, the deacetylation of **34** with alkali produced **36** in moderate yield. Preliminary studies in our laboratory have indicated that the dihydro diol **21** is the major metabolite whereas the dihydro diol **30** and the benzo[*f*]quinoline-5,6-diol are the minor metabolites when benzo[*f*]quinoline **1** is incubated with 3-methylcholanthrene-induced rat liver microsomes. The results of these studies and the tumorigenic and mutagenic activities of the dihydro diols and diol epoxides of **1** will be reported elsewhere.

Experimental Section

Ultraviolet spectra were recorded on a Perkin-Elmer Model Lambda-3 UV-vis spectrophotometer. ^{1}H NMR spectra were recorded on JOEL-270 FX and Bruker WF-360 spectrometers. The NMR facilities of the State University of New York at Buffalo and of the Syracuse University were used for obtaining 270 MHz and 360 MHz spectra, respectively. Unless noted otherwise, $CDCl_3$ was used as the solvent. Coumpling constants (J) are recorded in hertz (Hz) and chemical shifts in parts per million (δ) with Me_4Si as an internal standard. Mass spectra were obtained on a KRATOS MS80RFA spectrometer in the Department of Biophysics, State University of New York, Buffalo. Elemental microanalyses were performed by the Galbraith Laboratories, Inc., Knoxville, TN. Dry column grade silica gel was purchased from the ICN Pharmaceuticals. Preparative silica gel plates were purchased from Analtech, Newark, DE. Melting points were uncorrected. The designation α and β are used to indicate relative stereochemistry.

***trans*-8-Bromo-7-hydroxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (8) and *trans*-9-Bromo-10-hydroxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (9).** A mixture of 7,8,9,10-tetrahydrobenzo[*f*]quinoline (**3**, 8.9 g, 49 mmol), *N*-bromosuccinimide (NBS, 8.6 g 49 mmol), and α,α'-azobis(isobutyronitrile) (AIBN, 50 mg) in dry CCl_4 (200 mL) was refluxed with stirring under argon for 30 min. The mixture was cooled to 10 °C and filtered, and the filtrate was concentrated under reduced pressure to yield a mixture of **3**, **4**, and **5** (12.7 g) which was stirred with LiF (12 g) and Li_2CO_3 (18 g) in redistilled HMPA (100 mL) at 80–85 °C for 90 min under argon. The reaction mixture was cooled to room temperature, diluted with ether (300 mL), and filtered. The filtrate was washed with water (5 × 100 mL), dried, and concentrated to give a dark oil which was passed through a short column of silica gel using CH_2Cl_2 as eluant to produce 8.2 g (92.5%) of a mixture of **3** (40%), **6** (35%), and **7** (25%).

The above mixture, *N*-bromoacetamide (NBA, 6.2 g), and 3 drops of concentrated HCl were dissolved in a mixture of THF (200 mL) and water (50 mL) and stirred at 0–5 °C under argon for 4 h. The mixture was diluted with water (150 mL) and extracted with EtOAc (2 × 200 mL). The combined EtOAc extracts were dried (Na_2SO_4) and concentrated in vacuo. The crude product, thus obtained, was chromatographed on silica gel using CH_2Cl_2 as an eluant to remove relatively nonpolar impurities. The final elution with acetone gave a mixture of bromo hydrins **8** and **9** (5 g, 37%). A small sample of bromo hydrins having very similar R_f values on TLC was separated by preparative TLC on silica gel using 4% methanol in chloroform as the developing solvent to give **8** [mp 165–167 °C dec; ^{1}H NMR (270 MHz) δ 8.92 (dd, H_3), 8.31 (d, H_1), 8.00 and 7.87 (two d, H_5 and H_6), 7.45 (dd, H_2), 5.07 (t, H_7), 4.47 (m, H_8), 3.40–3.15 (m, 2 H), 2.80 (d, OH), 2.76–2.66 (m, 1 H), 2.50–2.35 (m, 1 H), $J_{1,2}$ = 8.61, $J_{1,3}$ = 1.65, $J_{2,3}$ = 4.3, $J_{5,6}$ = 8.5, $J_{7,8}$ = 4.6, $J_{7,OH}$ = 4.6.] and **9** [mp 166–168 °C dec; ^{1}H NMR (270 MHz) δ 8.79 (dd, H_3), 8.53 (d, H_1), 7.95 (d, 1 H), 7.46–7.40 (m, 2 H), 5.52 (br s, H_{10}), 4.69 (m, H_9), 3.45–3.21 (m, H_{7eq}), 3.0–2.91 (m, H_{7ax} and OH), 2.54–2.47 (m, H_{8eq}), 2.28–2.0 (m, H_{8ax}), $J_{1,2}$ = 8.24, $J_{2,3}$ = 4.3, $J_{1,3}$ = 1.3, $J_{5,6}$ = 8.5, J_{7gem} = 17.5, $J_{9,8eq}$ = 2.5, $J_{9,8ax}$ = 5.0, $J_{9,10}$ = 2.5.].

***trans*-7,8-Diacetoxy- and *trans*-9,10-Diacetoxy-7,8,9,10-tetrahydrobenzo[*f*]quinolines (14 and 15). Method I.** To a stirred solution of a mixture of bromo hydrins **8** and **9** (4.5 g, 16 mmol) in acetone (200 mL) was added 10% NaOH (50 mL) under argon. The mixture was stirred for 30 min and extracted with ether (2 × 200 mL). The combined ether extracts were washed with water (1 × 100 mL), dried (Na_2SO_4), and evaporated under reduced pressure to produce a mixture of tetrahydro epoxides **10** and **11**. This mixture was stirred with formic acid (30 mL) at 70–75 °C for 90 min under argon, and the mixture was then cooled to 0 °C, basified with aqueous NH_4OH, and extracted with EtOAc (3 × 100 mL). The combined EtOAc extracts were washed with water (1 × 100 mL), dried (Na_2SO_4) and concentrated under reduced pressure to yield 3.1 g (90% yield based on **8** and **9**, 32.6% yield based on **3**) of tetrahydro diols **12** and **13**.

The above mixture of tetrahydro diols **12** and **13** (3.0 g) was dissolved in Ac_2O (50 mL) and dry pyridine (4.5 mL) and stirred at room temperature for 12 h under argon. The mixture was basified with a cold solution of saturated Na_2CO_3 and then extracted with EtOAc (2 × 100 mL). The combined EtOAc extracts were washed with water (1 × 100 mL), dried (Na_2SO_4), and distilled in vacuo to yield 3.4 g (82.9%) of a solid residue which was chromatographed on dry column grade silica gel using petroleum ether–ether (2:3) as an eluant to obtain **15** (1.13 g) as a colorless crystalline solid: mp 148–149 °C (EtOAc/hexane); ^{1}H NMR (360 MHz) δ 8.89 (d, H_3) 8.17 (d, H_1), 8.05 and 7.52 (two d, H_5 and H_6), 7.44 (dd, H_2), 6.50 (d, H_{10}), 5.32 (m, H_9), 2.95–3.10 (m, H_7), 2.09–2.24 (m, H_8), 2.08 (s, 3 H), 2.01 (s, 3 H), $J_{1,2}$ = 8.5, $J_{2,3}$ = 4.3, $J_{5,6}$ = 8.6, $J_{9,10}$ = 3, $J_{8,9}$ = 3. Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.22; H, 5.68; N, 4.68. Found: C, 68.25; H, 5.63; N, 4.75. Further elution of the column gave **14** (0.83 g) as colorless crystalline solid: mp 160–161 °C (EtOAc/hexane); ^{1}H NMR (360 MHz) δ 8.94 (dd, H_3), 8.35 (d, H_1), 8.00 (d, 1 H), 7.55 (d, 1 H), 7.47 (dd, H_2), 6.20 (d, H_7), 5.26–5.30 (m, H_8), 3.23–3.29 (m, H_{10}), 2.22–2.33 (m, H_9), 2.15 (s, 3 H), 2.08 (s, 3 H), $J_{1,2}$ = 8.5, $J_{2,3}$ = 4.3, $J_{1,3}$ = 1.2, $J_{5,6}$ = 8.5, $J_{7,8}$ = 5.5. Anal. Calcd for $C_{17}H_{17}NO_4$: C,

68.22; H, 5.68; N, 4.68. Found: C, 68.03; H, 5.56; N, 4.66.

Method II. A mixture of silver benzoate (0.958 g, 4.2 mmol) and iodine (1.06 g, 4.2 mmol) was stirred in dry benzene (100 mL) under argon at room temperature. After 15 min, a solution of alkenes **6** and **7** (0.760 g, 4.2 mmol) in dry benzene (10 mL) was added, and the resulting reaction mixture was then refluxed for 24 h. The reaction mixture was filtered and the residue was washed with dry benzene. The filterate was distilled in vacuo to obtain a crude mixture of **16** and **17** which was then stirred in MeOH (50 mL) and sodium hydroxide (10 mL, 20%) at 0 °C for 4 h. Most of the methanol was distilled under reduced pressure and the residue was extracted with methylene chloride (5 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated under reduced pressure to obtain 0.534 g of the crude product. It was triturated repeatedly with ether to produce pure 130 mg (13.2%, based on **3**) of a mixture of **12** and **13**, which was then acetylated and separated as described in Method I.

***trans*-7,8-Diacetoxy-7,8-dihydrobenzo[*f*]quinoline (20).** A mixture of **14** (0.82 g, 2.74 mmol), NBS (0.48 g, 2.74 mmol), and α,α'-azobis(butyronitrile) (10 mg) in dry CCl_4 (60 mL) was stirred at 70–75 °C under argon for 30 min. The reaction mixture was cooled to 0 °C and filtered. The filterate was concentrated in vacuo and the resulting mixture of isomeric bromides **18** and **19** was triturated with ether to give yellow crystalline solid of **18**: mp 135–136 °C; ^{1}H NMR (270 MHz) δ 8.95 (d, H_3), 8.52 (d, H_1), 8.10 and 7.44 (two d, H_5 and H_6), 7.56 (dd, H_2), 6.47 (d, H_7), 5.88–5.99 (m, H_{10} and H_8), 2.81–2.88 (m, H_{9eq}), 2.53–2.58 (m, H_{9ax}), 2.23 (s, 3 H), 2.12 (s, 3 H), $J_{1,2}$ = 8.57, $J_{2,3}$ = 3.95, $J_{5,6}$ = 8.9, $J_{7,8}$ = 8.5, $J_{8,9ax}$ = 11.5, $J_{8,9eq}$ = 3.5, J_{9gem} = 14.0, $J_{9ax,10}$ = 3.3, $J_{9eq,10}$ = 3.3; mass spectrum, *m/e* 378, 380 (M^+ + H).

Thereafter the two methods were followed to prepare compound **20**.

Method A. A mixture of **18** (or **18** and **19**, 1.0 g), LiF (2.0), and Li_2CO_3 (3.0 g) in distilled HMPA (30 mL) was heated at 80–85 °C for 90 min. The reaction mixture was worked up as described for **6** and **7**. The crude product was purified on eight silica gel plates (20 cm × 20 cm × 1 mm) using ether as a developing solvent to get 570 mg (70%) of **20**: mp 145–146 °C (EtOAc/hexane); ^{1}H NMR (270 MHz) δ 8.96 (dd, H_3), 8.49 (d, H_1), 8.07 and 7.70 (two d, H_5 and H_6), 7.48 (dd, H_2), 7.39 (d, H_{10}), 6.34 (d, H_7), 6.30 (dd, H_9), 5.66 (dd, H_8), 2.12 (s, 3 H), 2.05 (s, 3 H), $J_{1,2}$ = 8.56, $J_{2,3}$ = 4.28, $J_{1,3}$ = 1.64, $J_{5,6}$ = 8.57, $J_{7,8}$ = 6.26, $J_{7,9}$ = 2.0, $J_{8,9}$ = 4.28, $J_{9,10}$ = 10.5. Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.01; N, 4.71. Found: C, 68.58; H, 5.07; N, 4.56.

Method B. A solution of **18** and **19** (200 mg, 0.5 mmol) and 1,5-diazabicyclo[4.3.0]non-5-ene (1 mL) in dry THF (20 mL) was kept for 12 h in the refrigerator (0–5 °C). Water (10 mL) was added to the reaction mixture which was then extracted with EtOAc (5 × 20 mL). The combined organic extracts were dried (Na_2SO_4) and distilled in vacuo to produce crude **20** which was chromatographed on two silica gel plates (20 cm × 20 cm × 1 mm) using ether as a developing solvent to yield 81 mg (57%) of **20**.

***trans*-7,8-Dihydroxy-7,8-dihydrobenzo[*f*]quinoline (21).** To a stirred solution of **20** (100 mg, 0.33 mmol) in methanol (20 mL) at 0 °C was added 5 mL of 2% sodium hydroxide solution. The reaction mixture was stirred for 15 min, concentrated under reduced pressure, and then extracted with ethyl acetate (3 × 10 mL). The combined EtOAc extracts were dried (Na_2SO_4) and rotaevaporated to produce **21** as a crystalline solid (21 mg, 29.5%): mp 250–251 °C; UV (5% THF in EtOH) δ_{max} (ϵ) 202 (31 600), 229 (29 324), 244 (33 700), 306 (5250, sh), 318 (6040), 325 (5690), 338 (3939); ^{1}H NMR (360 MHz, Me_2SO-d_6) δ 8.87 (d, H_3), 8.66 (d, H_1), 7.96 and 7.92 (two d, H_5 and H_6), 7.52 (dd, H_2), 7.24 (d, H_{10}), 6.18 (dd, H_9), 5.63 (d, OH_8), 5.25 (d, OH_7), 4.73 (dd, H_7), 4.35 (d, H_8), $J_{1,2}$ = 8.55, $J_{2,3}$ = 4.27, $J_{5,6}$ = 8.55, $J_{7,8}$ = 9.76, $J_{8,9}$ = 2.44, $J_{9,10}$ = 9.76, $J_{7,OH}$ = 6.10, $J_{8,OH}$ = 3.66; mass spectrum, *m/e* 213 (M^+), 195 ($M^+ - H_2O$).

(±)-7β,8α-Dihydroxy-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline 4-Oxide (23). A solution of dihydro diol **21** (22 mg, 0.1 mmol) and *m*-chloroperoxybenzoic acid (200 mg) in dry THF (150 mL) was stirred for 24 h at 25 °C under argon. The solvent was distilled in vacuo and the residue was triturated with ether and filtered, and the solid was washed repeatedly with ether and ethyl acetate to produce **23** as colorless crystalline solid (21 mg, 85.7%): mp 200 °C dec; UV (THF) λ_{max} (ϵ) 368 (4100, sh), 353 (5700), 338 (5000, sh), 254 (12 000), 246 (13 400); ^{1}H NMR (270 MHz, Me_2SO-d_6) δ 8.65–8.55 (m, H_1 and H_3), 8.48 and 8.07 (two d, H_5 and H_6), 7.53 (m, H_2), 5.98 (d, OH_7), 5.73 (d, OH_8), 4.92 (d, H_{10}), 4.45 (m, H_7), 3.86 (m, H_8), 3.76 (d, H_9), $J_{5,6}$ = 9.0, $J_{7,OH}$ = 6.2, $J_{7,8}$ = 6.92, $J_{8,OH}$ = 5.28, $J_{8,9}$ = 0, $J_{9,10}$ = 4.30; mass spectrum, *m/e* 245 (M^+), 227 ($M^+ - H_2O$), 211 ($M^+ - H_2O$ – O, base peak).

(±)-7β,8α-Diacetoxy-9α-bromo-10β-hydroxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (24). To a stirred solution of **20** (650 mg, 2.18 mmol) and NBA (310 mg, 2.24 mmol) in THF (50 mL) and H_2O (10 mL) was added a drop of concentrated HCl at 0 °C under argon. The progress of the reaction was monitored by silica gel TLC (5% MeOH in CH_2Cl_2). After the reaction was complete (3 h), H_2O (10 mL) and EtOAc (150 mL) were added. The organic layer was separated and washed with H_2O (10 mL), dried (Na_2SO_4), and distilled under reduced pressure to obtain a crude product which was triturated with ether and filtered to give 467 mg of pure **24**. The filterate was concentrated and purified on two silica gel plates (20 cm × 20 cm × 1 mm) using 5% MeOH in CH_2Cl_2 to obtain an additional 82 mg of pure **24**: total yield, 549 mg (64%); mp 223–224 °C; ^{1}H NMR (270 MHz) δ 8.93 (dd, H_3), 8.59 (d, H_1), 8.10 and 7.54 (two d, H_5 and H_6), 7.53 (dd, H_2), 6.40 (d, H_7), 5.76 (dd, H_8), 5.72 (dd , H_{10}), 4.79 (dd, H_9), 3.50 (d, OH), 2.16 (s, 3 H), 2.15 (s, 3 H), $J_{1,2}$ = 8.9, $J_{2,3}$ = 4.28, $J_{1,3}$ = 1.65, $J_{5,6}$ = 8.57, $J_{7,8}$ = 7.58, $J_{8,9}$ = 2.8, $J_{9,10}$ = 3.95, $J_{10,OH}$ = 6.48; mass spectrum, *m/e* 393 (M^+) and 395 (M^+).

(±)-7β,8α-Diacetoxy-9β,10β-epoxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (25). A solution of **24** (60 mg, 0.15 mmol) in dry THF (50 mL) was stirred with Amberlite (1 g) at 25 °C under argon for 8 h. The reaction mixture was filtered and the residue was washed with dry THF (4 × 5 mL). The combined THF filtrates were concentrated under reduced pressure to get a crude product which was chromatographed on a silica gel plate (20 cm × 20 cm × 1 mm) using 5% MeOH in CH_2Cl_2 as an eluant to obtain pure **24** (25 mg, 53%) as a crystalline solid: mp 166–168 °C; ^{1}H NMR (270 MHz) δ 9.0 (d, H_3), 8.66 (d, H_1), 8.16 and 7.73 (two d, H_5 and H_6), 7.55 (dd, H_2), 6.25 (m, H_7), 5.57 (m, H_8), 4.68 (d, H_{10}), 3.97 (m, H_9), 2.12 (s, 3 H), 2.06 (s, 3 H), $J_{1,2}$ = 8.57, $J_{2,3}$ = 4.29, $J_{5,6}$ = 8.57, $J_{7,8}$ = 3.3, $J_{7,9}$ = 1.3, $J_{8,9}$ = 2.3, $J_{9,10}$ = 3.63; high resolution mass spectrum obsd 314.1022 (M^+ + H), calcd 314.1028.

(±)-7β,8α-Dihydroxy-9β,10β-epoxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (26). To a stirred solution of **25** (36 mg, 0.11 mmol) in MeOH (5 mL) was added sodium hydroxide (1 mL, 5%) at 0 °C under argon. The reaction mixture was stirred for an additional 15 min at 0 °C. Cold water (5 mL) was added to the reaction mixture extracted with EtOAc (5 × 10 mL). The combined organic extracts were dried (Na_2SO_4) and distilled under reduced pressure to give a residue which was triturated with ether and filtered to produce 18 mg (72%) of **26**: mp 214 °C dec; UV (THF) λ_{max} (ϵ) 320 (2400), 308 (2600), 284 (3800), 240 (3900); ^{1}H NMR (270 MHz, Me_2SO-d_6) δ 8.94 (d, H_3), 8.82 (d, H_1), 8.05 and 7.85 (two d, H_5 and H_6), 7.63 (dd, H_2), 5.67 (d, OH), 5.15 (d, OH), 4.71 (d, H_{10}), 4.68 (dd, H_7), 3.90 (dd, H_8), 3.75 (d, H_9), $J_{1,2}$ = 8.57, $J_{2,3}$ = 4.28, $J_{5,6}$ = 8.57, $J_{7,8}$ = 5.6, $J_{9,10}$ = 3.96; mass spectrum, *m/e* 229 (M^+), 211 ($M^+ - H_2O$).

***trans*-9,10-Diacetoxy-7,7-dibromo-7,8,9,10-tetrahydrobenzo[*f*]quinoline (27) and *trans*-9,10-Diacetoxy-7-bromo-7,8,9,10-tetrahydrobenzo[*f*]quinoline (28).** A stirred solution of **15** (0.1 g, 0.33 mmol) was treated with NBS (60 mg) in the presence of AIBN as described with **14**. The crude product, thus obtained, was purified on two silica gel plates (20 cm × 20 cm × 1 mm) using ether as an eluant to obtain **27** (11 mg, 7.2%): mp 160 °C; ^{1}H NMR (270 MHz) δ 8.97 (d, H_3), 8.15–8.45 (m, H_6, H_5 and H_1), 7.51 (dd, H_2), 6.60 (d, H_{10}), 5.25–5.28 (m, H_9), 3.73 (br dd, $H_{8'}$), 3.55 (dd, H_8), 2.10 (s, 3 H), 2.03 (s, 3 H), $J_{1,2}$ = 8.57, $J_{2,3}$ = 4.29, $J_{5,6}$ = 9.22, $J_{8,8'}$ = 15.33, $J_{8',9}$ = 5.0, $J_{8',10}$ = 1, $J_{8,9}$ = 2.64, $J_{9,10}$ = 3.3.] and **28** (66 mg, 52.4%) [mp 164–165 °C; ^{1}H NMR (270 MHz, Me_2SO-d_6) δ 8.97 (d, H_3), 8.19 (d, H_1), 8.09 and 7.84 (two d, H_5 and H_6), 7.77 (dd, H_2), 6.46 (d, H_{10}), 6.06 (br s, H_7), 5.35 (br s, H_9), 2.77–2.50 (m, H_8), 2.03 (s, 3 H), 2.0 (s, 3 H), $J_{1,2}$ = 8.24, $J_{2,3}$ = 4.0, $J_{5,6}$ = 8.9, $J_{9,10}$ = 2.0; mass spectrum, *m/e* 378 (M^+ + H), 380 (M^+ + H).

***trans*-9,10-Diacetoxy-9,10-dihydrobenzo[*f*]qinoline (29a) and 7-Bromo-*trans*-9,10-diacetoxy-9,10-dihydrobenzo[*f*]-quinoline (29d).** The crude reaction product containing a mixture of **27** and **28** obtained by bromination of **15** (0.598 g, 2 mmol) was

treated with LiF (2 g) and Li_2CO_3 (3 g) in HMPA (10 mL) at 80–85 °C for 90 min, and the reaction mixture was worked up as described for **20**. The crude product was purified on ten silica gel plates (20 cm × 20 cm × 1 mm) using ether as a developing solvent to get **29a** (362 mg, 60.9%): mp 135–136 °C (EtOAc/hexane); ^{1}H NMR (360 MHz) δ 8.9 (d, H_3), 8.44 (d, H_1), 8.14 and 7.60 (two d, H_5 and H_6), 7.47 (dd, H_2), 6.90 (d, H_7), 6.73 (s, H_{10}), 6.30 (dd, H_8), 5.40 (dd, H_9), 2.03 (s, 3 H), 2.00 (s, 3 H), $J_{1,2}$ = 8.73, $J_{2,3}$ = 4.88, $J_{5,6}$ = 7.32, $J_{7,8}$ = 9.76, $J_{8,9}$ = 4.41, $J_{9,10}$ = 0. Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.98; H, 5.01; N, 4.71. Found: C, 68.51; H, 5.38; N, 4.89.] and **29d** (39 mg, 5%) [mp 150–151 °C (EtOAc/hexane); ^{1}H NMR (270 MHz) δ 8.95 (dd, H_3) 8.46 (d, H_1), 8.21 and 8.20 (two d, H_5 and H_6), 7.51 (dd, H_2), 6.76 (d, H_8), 6.71 (s, H_{10}), 5.30 (dd, H_9), 2.17 (s, 3 H), and 2.16 (s, 3 H); $J_{1,2}$ = 8.5, $J_{2,3}$ = 4.29, $J_{5,6}$ = 8.9, $J_{8,9}$ = 6.26, $J_{9,10}$ = 2.0.].

7-Bromo-*trans*-9,10-diacetoxy-9,10-dihydrobenzo[*f*]quinoline (29d), *trans*-9,10-Diacetoxy-9,10-dihydrobenzo[*f*]quinoline (29a), *trans*-10-Acetoxy-9-hydroxy-9,10-dihydrobenzo[*f*]quinoline (29b), and *trans*-9-Acetoxy-10-hydroxy-9,10-dihydrobenzo[*f*]quinoline (29c). The crude reaction product, obtained by bromination of **15** (0.935 g, 3.1 mmol), was treated with DBN (1 mL) in dry THF (30 mL) and was worked up as described for **20**. The crude product was chromatographed on ten silica gel plates (20 cm × 20 cm × 1 mm) using ether as an eluant to obtain **29d** (40 mg, 4%), **29a** (275 mg, 29.9%), and a mixture of **29b** and **29c** (108 mg, 13.6%). The ^{1}H NMR spectrum of the mixture of **29b** and **29c** showed that they were in a ratio of 4:3.

***trans*-9,10-Dihydroxy-9,10-dihydrobenzo[*f*]quinoline (30).** Hydrolysis of **29a** (0.326 g, 1.1 mmol) was performed with sodium hydroxide (15 mL) in methanol (60 mL) as described for **21** to produce 147 mg (62.8%) of **30**: mp 245–247 °C; UV (5% THF in EtOH) λ_{max} (ε) 204 (23634), 223 (16631), 253 (29249), 293 (3210, sh), 302 (3793), 314 (4085), 330 (3939), 345 (3640); ^{1}H NMR (360 MHz, Me_2SO-d_6) δ 8.85 (d, H_3), 8.62 (d, H_1), 7.94 and 7.62 (two d, H_5 and H_6), 7.56 (dd, H_2), 6.72 (d, H_7), 6.22 (dd, H_8), 5.25 (d, OH_{10}), 5.15 (br s, H_{10}), 4.97 (d, OH_9), 4.21 (br s, H_9), $J_{1,2}$ = 8.54, $J_{2,3}$ = 3.6, $J_{5,6}$ = 8.54, $J_{7,8}$ = 9.15, $J_{8,9}$ = 4.89, $J_{9,10}$ = 0, $J_{9,OH}$ = 4.88, $J_{10,OH}$ = 6.1; mass spectrum, *m/e* 213 (M^+), 195 ($M^+ - H_2O$).

9α,10β-Diacetoxy-7α,8β-dibromo-7,8,9,10-tetrahydrobenzo[*f*]quinoline (31), 9α,10β-Diacetoxy-8β-bromo-7α-hydroxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (32), and 9α,10β-Diacetoxy-8α-bromo-7β-hydroxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (33). The reaction of **29a** (0.66 g, 2.2 mmol) was carried out with NBA (0.372 g, 2.7 mmol) in presence of HCl as described in the preparation of **24**. The crude reaction product was triturated with ether and filtered. The solid thus obtained (235 mg, 23.5%) was pure **31**: mp 247 °C (MeOH); ^{1}H NMR (270 MHz, Me_2SO-d_6) δ 9.16 (br s, H_3), 8.42 (d, H_1), 8.25 and 8.15 (two d, H_5 and H_6), 7.91 (dd, H_2), 6.78 (d, H_{10}), 5.71 (dd, H_9), 5.15 (d, H_7), 4.41 (t, H_8), 2.1 (s, 3 H), 1.97 (s, 3 H), $J_{1,2}$ = 8.57, $J_{2,3}$ = 4.61, $J_{5,6}$ = 8.57, $J_{7,8}$ = 10.0, $J_{8,9}$ = 9.55, $J_{9,10}$ = 5.6.

The filterate was concentrated under reduced pressure and chromographed on ten silica gel plates (20 cm × 20 cm × 1 mm) to obtain a mixture of **32** and **33** (420 mg, 48.5%) in a ratio of 6:1 as determined from the ^{1}H NMR spectrum of the mixture (H_{10} of **32** and **35** at 6.73 and 6.60, respectively). The solid compound was repeatedly recrystallized from EtOAc and hexane to produce a pure sample of **32**: mp 175 °C; ^{1}H NMR (270 MHz) δ 8.95 (d, H_3), 8.20 (d, H_1), 8.10 (t, H_5 and H_6), 7.45 (dd, H_2), 6.73 (d, H_{10}), 5.76 (d, H_9), 5.22 (dd, H_7), 4.24 (t, H_8), 3.22 (d, OH), 2.18 (s, 3 H), 2.04 (s, 3 H), $J_{1,2}$ = 8.57, $J_{2,3}$ = 3.95, $J_{5,6}$ = 8.24, $J_{7,8}$ = 9.56, $J_{7,OH}$ = 4.29, $J_{8,9}$ = 10.22, $J_{9,10}$ = 4.6; mass spectrum, *m/e* 393, 395 (M^+).

Although **33** could not be obtained as a pure compound even after several repeated recrystallizations, the following ^{1}H NMR pattern could be easily figured out from the ^{1}H NMR spectrum of the mixture of **32** and **33**: ^{1}H NMR (270 MHz) δ 8.95 (d, H_3), 8.22–8.10 (m, H_1, H_5 and H_6), 7.45 (dd, H_2), 6.60 (d, H_{10}), 5.79–5.70 (m, H_9), 5.25–5.20 (m, H_7), 4.72 (dd, H_8), 3.14 (d, OH), 2.10 (s, 3 H), 2.08 (s, 3 H), $J_{7,8}$ = 8.90, $J_{8,9}$ = 2.31, $J_{9,10}$ = 3.29.

(±)-9α,10β-Diacetoxy-7α,8α-epoxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (34) and 9α,10β-Diacetoxy-7β,8β-epoxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (35). To a stirred solution of **32** and **33** (0.14 g, 0.35 mmol) and *n*-Bu_4N^+ HSO_4^- (50 mg) in methylene chloride (50 m) was added a saturated solution of Na_2CO_3 (5 mL) at 25 °C, and the reaction mixture was vigorously stirred for additional 75 min. The organic layer was separated and washed with water (2 × 5 mL), dried (Na_2SO_4), and rotaevaporated. The residue, thus obtained, was triturated with ether several times and the combined ether triturates were concentrated under reduced pressure to produce a crude mixture. This crude mixture was chromotographed on two silica gel plates (20 cm × 20 cm × 1 mm) using 4% MeOH in $CHCl_3$ as a developing solvent to produce 87 mg (79.8%) of the mixture of **34** and **35**. Repeated recrystallization of this mixture from ethyl acetate–petroleum ether gave pure **34**: mp 162–163 °C (EtOAc/hexane); ^{1}H NMR (270 MHz) δ 8.96 (dd, H_3), 8.28 (d, H_1), 8.18 and 7.88 (two d, H_6 and H_5), 7.45 (dd, H_2), 6.57 (d, H_{10}), 5.65 (dd, H_9), 4.16 (d, H_7), 3.98 (dd, H_8), 2.13 (s, 3 H), 2.07 (s, 3 H), $J_{1,2}$ = 8.57, $J_{2,3}$ = 4.29, $J_{1,3}$ = 1.65, $J_{5,6}$ = 8.57, $J_{7,8}$ = 4.29, $J_{8,9}$ = 1.98, $J_{9,10}$ = 4.30; high resolution mass spectrum, obsd 314.1022, calcd 314.1028.

Compound **35** could not be isolated in pure form by repeated crystallizations. However, the following ^{1}H NMR spectrum pattern could be easily figured out from the spectrum of the mixture of **34** and **35**: ^{1}H NMR of **35** (270 MHz) δ 8.97 (d, H_1), 8.30 (d, H_1), 8.25 and 7.95 (two d, H_6 and H_5), 7.50 (dd, H_2), 6.75 (br s, H_{10}), 5.70 (br s, H_9), 4.14 (d, H_7), 3.96 (m, H_8), 2.11 (s, 3 H), 2.01 (s, 3 H); $J_{7,8}$ = 4.32, $J_{8,9}$ = $J_{8,9}$ = 1.

(±)-9α,10β-Dihydroxy-7α,8α-epoxy-7,8,9,10-tetrahydrobenzo[*f*]quinoline (36). To a stirred solution of **34** (28 mg, 0.08 mmol) in THF (2 mL) and MeOH (1 mL) was added 0.5 mL of NaOH (5%) at 0 °C. The reaction mixture was stirred for 10 min at 0 °C and then the solvent was removed under pressure. The residue was treated with H_2O (2 mL) and filtered. The solid, thus obtained, was washed with acetone (2 × 2 mL) to obtain pure **36** (9 mg, 45%): mp 241 °C dec; UV (THF) λ_{max} (ε) 320 (1950), 314 (1400), 308 (2000), 280 (2700), 240 (5700); ^{1}H NMR (270 MHz, Me_2SO-d_6) δ 9.30 (d, H_1), 8.55 (d, H_3), 7.95 and 7.88 (two d, H_5 and H_6), 7.46 (dd, H_2), 5.76 (d, OH_{10}), 5.60 (d, OH_9), 4.86 (dd, H_{10}), 4.20 (d, H_7), 4.00 (m, H_9), 3.78 (d, H_8); $J_{1,2}$ = 8.57, $J_{2,3}$ = 3.95, $J_{5,6}$ = 8.57, $J_{7,8}$ = 4.28, $J_{8,9}$ = 1, $J_{9,10}$ = 7.02, $J_{9,OH}$ = 5.4, $J_{10,OH}$ = 7.02.

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Registry No. **3**, 80028-83-7; **4**, 103620-41-3; **5**, 103620-42-4; **6**, 103620-13-9; **7**, 103620-14-0; (±)-**8**, 103620-15-1; (±)-**9**, 103620-16-2; (±)-**10**, 103620-17-3; (±)-**11**, 103620-18-4; (±)-**12**, 103620-19-5; (±)-**13**, 103620-20-8; (±)-**14**, 103620-21-9; (±)-**15**, 103620-22-0; (±)-**16**, 103620-23-1; (±)-**17**, 103620-24-2; (±)-**18**, 103620-25-3; (±)-**19**, 103667-11-4; (±)-**20**, 103639-19-6; (±)-**21**, 103620-26-4; (±)-**23**, 103620-27-5; (±)-**24**, 103620-28-6; (±)-**25**, 103620-29-7; (±)-**26**, 103620-30-0; (±)-**27**, 103620-31-1; **28**, 103620-32-2; (±)-**29a**, 103620-33-3; (±)-**29b**, 103620-34-4; (±)-**29c**, 103620-35-5; (±)-**29d**, 103620-36-6; (±)-**30**, 103667-12-5; (±)-**31**, 103620-37-7; (±)-**32**, 103620-38-8; (±)-**33**, 103667-13-6; (±)-**34**, 103620-39-9; (±)-**35**, 103667-14-7; (±)-**36**, 103620-40-2.