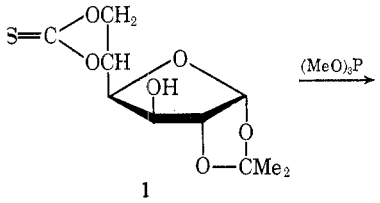
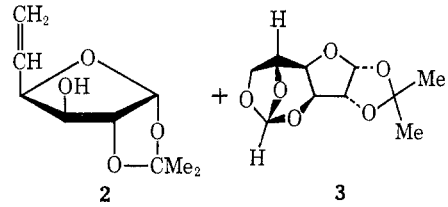
The structure of **3** is fully supported by 100-MHz nmr spectral assignments verified by spin decoupling, and by mass spectrometry; a major ion having *m/e* 215 corresponding to loss of a methyl radical from the molecular ion is observed. Full spectral details are recorded in the Experimental Section, where 100-MHz nmr data verified by spin decoupling are also recorded for the thionocarbonate **1**, together with mass spectral data.

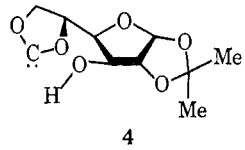


1



2 major + **3** minor

The formation of the orthoformate **3** as a side product in the conversion of thionocarbonate **1** into alkene **2** can be attributed to the intramolecular insertion of a carbene intermediate (**4**) into the O–H bond of the hydroxyl group at C-3, and provides strong evidence that the same carbene **4** is an intermediate in formation of the alkene **2**. It would be difficult to reconcile the observed formation of **3** as a side product if a reaction intermediate of the ylide type were involved in the conversion of **1** into **2**.



4

Experimental Section

General Methods.—Nmr spectra were measured at 100 MHz, and chemical shifts refer to an internal standard of tetramethylsilane (τ 10.00); the latter also provided a lock signal. Signal assignments were verified by spin decoupling. Deuteration was performed by adding 1 drop of deuterium oxide to the prepared sample. Mass spectra were recorded by C. R. Weisenberger with an AEI MS-902 high-resolution, double-focusing spectrometer with an accelerating potential of 8 kV, an ionizing potential of 70 eV, and a direct-insertion probe with an inlet temperature of 250°. Thin layer chromatography (tlc) was performed with 0.25-mm layers of silica gel G (E. Merck, Darmstadt, Germany) activated at 120° as the adsorbent and sulfuric acid as the indicator.

1,2-*O*-Isopropylidene-α-D-glucofuranose 5,6-Thionocarbonate (1).—This compound was prepared as described previously,[5] mp 205–206°, $[\alpha]^{20}D$ −18° (*c* 1, acetone); 100-MHz nmr data in acetone-d_6 τ 3.98 (1-proton doublet, $J_{1,2}$ = 3.4 Hz, H-1), 4.62 (1-proton, symmetrical eight-line multiplet, $J_{4,5}$ = 2.6 Hz, H-5), 5.26 (2-proton, apparent doublet, $J_{5,6} \sim 8$ Hz, H-6,6′), 5.37 (1-proton triplet, $J_{3,4}$ = 3.5 Hz, H-4), 5.46 (1-proton doublet, $J_{2,3} \sim 0$ Hz, H-2), 5.68 (1-proton, broad peak, becoming a doublet after deuteration, H-3), 7.12 (1-proton, broad peak, disappears on deuteration, OH), 8.58, 8.75 (3-proton singlets, CMe_2); mass spectral data (relative peak intensity and assignment in parentheses) *m/e* 262 (1, M^+), 247 (1, M − CH_3), 187 (65, M − CH_3 − CH_3CO_2H), 159 (6), 129 (9), 127 (18), 101 (9), 100 (4), 86 (42), 85 (90), 73 (20), 71 (15), 69 (34), 68 (5), 60 (100, $CH_3CO_2H \cdot^+$), 59 (100, $CH_3COCH_3H^+$), 58 (20), 57 (27), 56 (5), 55 (25), 45 (14), 44 (10), 43 (60, CH_3CO^+).

Reaction of 1 with Trimethyl Phosphite.—The following is an adaptation of an earlier procedure.[5] A solution of **1** (5.0 g, 19 mmol) in freshly distilled trimethyl phosphite (20 ml) was heated to reflux under an atmosphere of nitrogen. The bath temperature was maintained for 60 hr at 150°, during which time the mixture ceased to reflux. The solution was cooled and poured into 250 ml of 1 *M* aqueous sodium hydroxide and the mixture was stirred vigorously until a permanently basic, homogeneous solution resulted. The solution was extracted with four 250-ml portions of chloroform, and the dried (magnesium sulfate) extract was evaporated to a colorless syrup (2.78 g) that crystallized spontaneously. Tlc of the product (3:1 dichloromethane–ether) showed a major component (**2**), R_f 0.5, and a minor component (**3**), R_f 0.9. The solid was dissolved in the minimum volume of ether, and Skellysolve[11] C (50 ml) was added. The solution was then concentrated at 15–20° until it became slightly turbid, whereupon it was seeded with **2** and refrigerated for 12 hr, to give **5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (2)**, yield 1.92 g (in two crops). The residual mother liquors were chromatographed on a column (3 × 30 cm) of silica gel (type 7734, 70–325 mesh ASTM, E. Merck) with 3:2 petroleum ether (bp 60–110°)–ether as eluent. The first product to be eluted was **1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-orthoformate (3)**, yield 50 mg (0.22 mmol, 1%), identical with an authentic sample of **3** by mixture melting point and ir and nmr spectra. Further elution of the column gave an additional 0.62 g of **2**, total yield of **2** 2.54 g (13 mmol, 72%), mp 61–65°, $[\alpha]^{20}D$ −60° (*c* 2, chloroform).

1,2-*O*-Isopropylidene-α-D-glucofuranose 3,5,6-Orthoformate (3).—Into a 25-ml flask was placed 1,2-*O*-isopropylidene-α-D-glucofuranose (5.0 g, 22.6 mmol) and triethyl orthoformate (3.4 ml, 22.6 mmol) and 1 ml of acetic acid. The mixture was heated under an atmosphere of nitrogen for 4 hr at 120°. The cooled mixture was evaporated and three 15-ml portions of toluene were evaporated from the residue to remove acetic acid. Sublimation of the resultant solid at 0.05 Torr and 120° gave a white powder that was recrystallized from ethyl acetate to give pure **3**, yield 4.9 g (21.2 mmol, 94%), mp 201–203°, $[\alpha]^{20}D$ −41.5° (*c* 0.3, chloroform); R_f 0.9 (3:1 dichloromethane–ether); nmr data in chloroform-*d* τ 3.94 (1-proton doublet, $J_{1,2}$ = 3.2 Hz, H-1), 4.03 (1-proton singlet, orthoformate CH), 5.22 (1-proton, broad multiplet, width 12 Hz, H-5), 5.44 (1-proton doublet, $J_{2,3} \sim 0$ Hz, H-2), 5.65 (1-proton doublet, $J_{3,4}$ = 3.0 Hz, H-3), 5.92 (1-proton doublet and 1-proton multiplet, $J_{6,6'}$ = 8.0 Hz, $J_{5,6} \sim 0$, H-6, H-4), 6.11 (1-proton quartet, $J_{5,6}$ = 4.6 Hz, H-6′), 8.52, 8.78 (3-proton singlets, CMe_2); mass spectral data (relative intensities and assignments given in parentheses) *m/e* 215 (60, M − CH_3), 187 (<1, M − CH_3CO), 159 (<1, M − 71), 155 (<1, M − CH_3 − CH_3CO_2H), 129 (70), 127 (20), 114 (5), 113 (15), 101 (20), 100 (50), 85 (85), 71 (10), 69 (21), 61 (11), 59 (41, $CH_3COCH_3H^+$), 43 (100, CH_3CO^+).

For this compound prepared by a different procedure the following constants have been reported:[10] mp 201–203°, $[\alpha]D$ −40.9° (chloroform), τ 3.90 (H-1), 3.99 (orthoformate CH).

Fusion of **3** (1 g) with triphenylacetic acid (0.1 g) at 210° led to quantitative recovery of unchanged **3**, which sublimed from the reaction vessel and no conversion[12] into **2** was observed.

Registry No.—**1**, 25356-81-4; **3**, 3891-47-2.

(11) Petroleum ether fractions, bp 90–97°, Skelly Oil Co., Kansas City, Mo.

(12) G. Crank and F. W. Eastwood, *Aust. J. Chem.*, **17**, 1392 (1964).

The Synthesis of Cherylline

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Received March 6, 1970

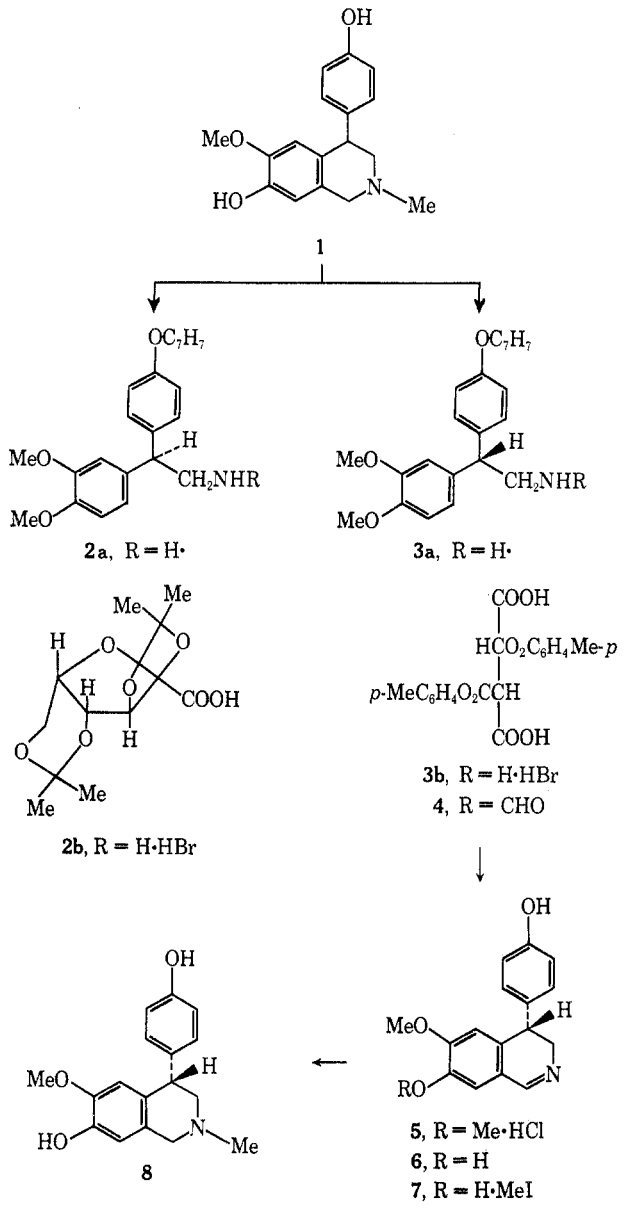
The isolation, structure, and *S* configuration of cherylline (**8**), a new representative of the rare phenolic *Amaryllidaceae* alkaloids, was recently reported[1] and

(1) A. Brossi, G. Grethe, S. Teitel, W. C. Wildman, and D. T. Bailey, *J. Org. Chem.*, **36**, 1100 (1970).

followed by a synthesis of (±)-cherylline.[2] We now describe the first total synthesis of the alkaloid **8** as well as its unnatural isomer.[3]

Resolution of the (±)-phenethylamine **1**[2] with (−)-diacetone-2-keto-L-gulonic acid[4] in 2-propanol afforded the diastereomeric salt **2a** (Scheme I). Treatment of

SCHEME I



the resulting mother liquors (as the free base) with (−)-di-O-*p*-toluoyl-D-tartaric acid in acetone provided the diastereomeric salt **3a**. Each of these was converted to the corresponding crystalline hydrobromides **2b** and **3b**[5] whose ORD and CD spectra were exact mirror images.

Reaction of the (−)-phenethylamine **3b** with methyl formate provided the (−)-N-formyl derivative **4** which was subjected to Bishler–Napieralski cyclization followed by debenzylation with concentrated hydrochloric acid at 25° to give the (−)-6,7-dimethoxydihydroisoquinoline **5**. Selective O-demethylation[6,7] of **5** with 48% hydrobromic acid at 100° for 6 hr yielded the (−)-6-methoxy-7-hydroxy derivative **6** which was converted with methyl iodide into the corresponding (−)-quaternary **7**. All of these levoratatory intermediates exhibited positive Cotton effects in their ORD spectra. However, sodium borohydride reduction of **7** was accompanied by inversion of the Cotton effects to afford (−)-cherylline (**8**) whose physical and spectral properties were identical with natural cherylline.[1,8] By the same reaction sequences, the (+)-phenethylamine **2b** was transformed into the unnatural isomer of cherylline.

(2) A. Brossi and S. Teitel, *Tetrahedron Lett.*, 417 (1970).

(3) Presented in part by one of us (A. B.) at the Third Natural Products Symposium in Mona, Jamaica, Jan 5–9, 1970.

(4) T. Reichstein and A. Grüssner, *Helv. Chim. Acta*, **17**, 311 (1934). Its potential as a resolving agent was first recognized by our colleagues, Drs. W. Leimgruber and E. Mohacsi of these laboratories.

(5) The optical purity of these two isomers could be better judged at $[\alpha]_{365}$ where the rotations were enhanced over those at $[\alpha]_D$.

Experimental Section[9]

(+)-2(*R*)-2-(4-Benzyloxyphenyl)-2-(3,4-dimethoxyphenyl)-ethylamine diacetone-2-keto-L-gulonate (2a) and Hydrobromide 2b.—An aqueous solution of 28.4 g (0.064 mol) of **1**·HBr[2] was rendered alkaline with 10% sodium hydroxide and extracted with methylene chloride, and the extract was evaporated. The residual oil and 18.7 g (0.064 mol) of (−)-diacetone-2-keto-L-gulonic acid hydrate[4] were dissolved in 185 ml of 2-propanol and stored at 25° for 17 hr. The crystals were filtered, dried (24.6 g), and recrystallized first from a mixture of 100 ml of methanol and 600 ml of 2-propanol, and then from a mixture of 75 ml of methanol and 300 ml of 2-propanol to give 13.2 g (64% based on 0.032 mol) of **2a**: mp 144–145°; $[\alpha]_D$ −5.2°.

Anal. Calcd for $C_{23}H_{25}NO_3 \cdot C_{12}H_{16}O_7$ (637.73): C, 65.92; H, 6.80. Found: C, 65.98; H, 6.80.

An aqueous solution of 12.8 g (0.02 mol) of **2a** was made alkaline with 10% sodium hydroxide and the free base was extracted with methylene chloride. The extract was rendered acidic with ethanolic hydrogen bromide and evaporated, and the residue was crystallized twice from acetonitrile, to give 7.5 g (84%) of **2b**: mp 123–125°; $[\alpha]_D$ +6.5°, $[\alpha]_{365}$ +21.0°; ORD (*c* 0.501, MeOH) $[\Phi]_{700}$ +16.4°, $[\Phi]_{589}$ +22.6°, $[\Phi]_{290}$ +355° (tr), $[\Phi]_{277}$ +800° (pk), $[\Phi]_{250}$ −1330° (tr), and $[\Phi]_{230}$ +6240° (pk); CD $[\theta]_{300}$ 0, $[\theta]_{287}$ −700, $[\theta]_{274}$ 0, $[\theta]_{270}$ +350, $[\theta]_{259}$ 0, and $[\theta]_{240}$ −17,600.

Anal. Calcd for $C_{23}H_{25}NO_3 \cdot HBr$ (444.39): C, 62.17, H, 5.90. Found: C, 62.42; H, 5.75.

(−)-2(*S*)-2-(4-Benzyloxyphenyl)-2-(3,4-dimethoxyphenyl)-ethylamine Di-O-*p*-toluoyl-D-tartrate (3a) and Hydrobromide (3b).—The 2-propanol mother liquors, obtained from the crystallization of crude **2a**, were evaporated, the residue dissolved in water, rendered alkaline with 10% sodium hydroxide, and extracted with methylene chloride. The organic extract was washed with 2% sodium hydroxide and evaporated. The residual oil (8.2 g) and 8.7 g (24.2 mmol) of (−)-di-O-*p*-toluoyl-D-

(6) Based on the preferential O-demethylation of the 7-methoxy group in 6,7-dimethoxy-3,4-dihydroisoquinoline with mineral acid as reported by H. Bruderer and A. Brossi, *Helv. Chim. Acta*, **48**, 1945 (1965).

(7) The partial ether cleavage of dimethoxy-substituted 3,4-dihydroisoquinolines and the application in certain alkaloid syntheses was presented by one of us (A. B.) at the 13th Symposium on the Chemistry of Natural Products, Sapporo, Japan, Sept 25–27, 1969, pp 177–186 of abstract, and will be detailed by A. Brossi and S. Teitel in a forthcoming publication.

(8) We are grateful to Professor W. C. Wildman of Iowa State University for providing us with a sample of natural cherylline.

(9) All melting points (corrected) were taken in open capillary tubes with a Thomas–Hoover melting apparatus. All thin layer chromatography employed silica gel G plates which were developed for 12–15 cm and detected with Dragendorff's reagent. The ultraviolet spectra were measured in ethanol with a Cary recording spectrophotometer Model 14M. Nuclear magnetic resonance spectra were obtained with a Varian Associates Model A-60 or HA-100 spectrophotometer using, unless noted otherwise, DMSO-d_6 as solvent and tetramethylsilane as internal reference. Chemical shifts are reported in δ with following abbreviations: (s) singlet, (m) multiplet, (t) triplet, (b) broad. Optical rotations were measured with a Perkin-Elmer polarimeter Model 141 using a 1% solution in methanol at 25°. Rotatory dispersion curves were determined at 23° with a Durrum-Jasco spectrophotometer Model 5 using 1 cm, 0.1 cm, or 0.1 mm cells. Circular dichroism curves were measured on the same instrument and are expressed in molecular ellipticity units $[\theta]$. The mass spectra were taken with a CEC 21-110 mass spectrometer at 70 eV using a direct insertion probe. Extracts of products in organic solvents were washed with water and dried over anhydrous sodium sulfate.

tartaric acid were dissolved in 100 ml of acetone; the solution was stored at 25° for 20 hr. The crystals were filtered and recrystallized twice from acetone to give 12 g (50% based on 0.032 mol present in 1) of **3a**: mp 184–185°; $[\alpha]_D$ −79.0°.

Anal. Calcd for $C_{23}H_{25}NO_3 \cdot C_{20}H_{18}O_8$ (749.78): C, 68.88; H, 5.78. Found: C, 68.63; H, 5.79.

Conversion of 7.5 g (0.01 mol) of **3a** by the procedure given for the preparation of **2b** afforded, after two crystallizations from acetonitrile, 3.8 g (86%) of **3b**: mp 122–124°; $[\alpha]_D$ −6.5°, $[\alpha]_{365}$ −20.9°; ORD and CD mirror images of **2b**.

Anal. Calcd for $C_{23}H_{25}NO_3 \cdot HBr$ (444.39): C, 62.17; H, 5.90. Found: C, 62.22; H, 5.55.

(−)-2(*S*)-N-[2-(4-Benzyloxyphenyl)-2-(3,4-dimethoxyphenyl)-ethyl Formamide (4).—An aqueous solution of 7.3 g (16.4 mmol) of **3b** was rendered alkaline with sodium hydroxide and extracted with methylene chloride, and the extract evaporated. The residue was dissolved in 200 ml of methyl formate and heated at 60–65° under 20 atmospheres of nitrogen for 24 hr. The volatiles were evaporated and the residue dissolved in benzene and chromatographed over 45 g of silica gel. The benzene and benzene–ethyl acetate (80:20) eluates (700 mg) were discarded and the benzene–ethyl acetate (50:50) eluates were collected and evaporated to give 5.8 g (90%) of **4** as a colorless oil: bp 140° (0.02 mm); $n^{25}D$ 1.5699; uv max 226 mμ (ε 22,360), 278 (5010), 284 (4420) (sh); nmr ($CDCl_3$) δ 3.82 (s, 6, OCH_3), 5.00 (s, 2, OCH_2), 5.58 (b, 1, NH), 6.60–7.50 (m, 7, aromatic), 7.34 (s, 5, C_6H_5), and 8.05 (s, 1, CHO); ORD and CD spectra the same as given for **3b**, within experimental error.

Anal. Calcd for $C_{24}H_{25}NO_4$ (391.45): C, 73.63; H, 6.44. Found: C, 73.55; H, 6.54.

(−)-4(*S*)-6,7-Dimethoxy-4-(4-hydroxyphenyl)-3,4-dihydroisoquinoline Hydrochloride (5).—A mixture of 16.4 g (42 mmol) of **4** and 18.6 ml of phosphorus oxychloride in 300 ml of acetonitrile was stirred and refluxed for 1 hr and evaporated under reduced pressure. The residue was suspended in 5% sodium hydroxide and extracted with ethyl acetate, and the extract evaporated. The residual oil (18 g) was dissolved in 150 ml of benzene, 150 ml of concentrated hydrochloric acid was added and the mixture was stirred vigorously at 25° for 15 hr and evaporated under reduced pressure. The residue was crystallized from a mixture of ethanol and ether to give 8.1 g (58%) of **5**·HCl: mp 221–222°; uv max 233 mμ (ε 19,350), 252 (15,000) (sh), 286 (5550), 310 (7400), and 363 (5150); nmr δ 3.80 (s, 3, OCH_3), 3.82 (s, 3, OCH_3), 4.06 (m, 2, CH_2), 4.48 (t, 1, J = 7 Hz, CH), 6.73, 6.90 (AA'BB', 4, aromatic), 6.87, 7.63 (2 s, 2, CH-7, 8), 9.08 (s, 1, CH=N), 9.55 (b, 1, OH or NH); $[\alpha]_D$ −139.5°; ORD (*c* 0.337, CH_3OH) $[\Phi]_{700}$ −309°, $[\Phi]_{589}$ −444°, $[\Phi]_{400}$ −495° (pk), $[\Phi]_{350}$ −13,870° (tr), $[\Phi]_{306}$ +8420° (pk), $[\Phi]_{272}$ −3960° (sh), $[\Phi]_{254}$ −17,330° (tr), and $[\Phi]_{230}$ +24,760° (pk); CD $[\theta]_{416}$ 0, $[\theta]_{376}$ +6530, $[\theta]_{356}$ 0, $[\theta]_{329}$ −16,990, $[\theta]_{302}$ 0, $[\theta]_{292}$ +3920, $[\theta]_{283}$ 0, $[\theta]_{272}$ −2610, $[\theta]_{266}$ −1310, $[\theta]_{244}$ −42,470, $[\theta]_{232}$ 0, and $[\theta]_{228}$ +16,340.

Anal. Calcd for $C_{17}H_{17}NO_3 \cdot HCl$ (319.79): C, 63.85; H, 5.67. Found: C, 64.06; H, 5.85.

(−)-4(*S*)-7-Hydroxy-4-(4-hydroxyphenyl)-6-methoxy-3,4-dihydroisoquinoline (6).—A solution of 11.0 g (34.5 mmol) of **5** in 300 ml of 48% hydrobromic acid was stirred at 100° for 6 hr and evaporated under reduced pressure. The residue was dissolved in water, neutralized with sodium bicarbonate, and extracted with ethyl acetate (four 125-ml portions). The extracts were evaporated and crystallized from a mixture of ethanol and ether to give 7.4 g (80%) of **6**: mp 207–208°; uv max 233 mμ (ε 30,700), 280 (8400), and 318 (5000); nmr δ 3.65 (s, 3, OCH_3-6), 6.45, 6.82 (s, 2, CH-5,8), 6.60, 6.86 (AA'BB', 4, CH-2',3',5',6'), 8.12 (b, 1, CH-1), and 9.03 (b, 2, OH); $[\alpha]_D$ −222.4°, ORD (*c* 0.507, 0.1 *N* HCl in CH_3OH) $[\Phi]_{700}$ −334°, $[\Phi]_{589}$ −468°, $[\Phi]_{406}$ +2390° (pk), $[\Phi]_{344}$ −10,620° (tr), $[\Phi]_{305}$ +10,360° (pk), $[\Phi]_{254}$ −10,090° (tr), and $[\Phi]_{230}$ +35,060° (pk); CD $[\theta]_{430}$ 0, $[\theta]_{380}$ +5260, $[\theta]_{360}$ 0, $[\theta]_{328}$ −16,480, $[\theta]_{302}$ 0, $[\theta]_{290}$ +2450, $[\theta]$ −2800 (sh), $[\theta]_{244}$ −30,140, $[0]_{231}$ 0, and $[0]_{228}$ +4210.

Anal. Calcd for $C_{16}H_{15}NO_3$ (269.29): C, 71.36; H, 5.61. Found: C, 71.22; H, 5.79.

(−)-4(*S*)-7-Hydroxy-4-(4-hydroxyphenyl)-6-methoxy-2-methyl-3,4-dihydroisoquinolinium Iodide (7).—A solution of 5.0 g (18.5 mmol) of **6** and 26 ml of methyl iodide in 300 ml of methanol was stored at 25° for 24 hr and evaporated. The residue was crystallized from a mixture of methanol and ether to give 5.3 g (69%) of **7**: mp 242–243°; uv max 215 mμ (ε 29,100), 251 (20,600), 280 (5900), 312 (10,000), and 370 (7300); nmr δ 3.63 (s, 3, $^+NCH_3$), 3.79 (s, 3, OCH_3), 4.08 (m, 2, CH_2), 4.53 (t, 1, J = 8 Hz, CH), 6.72, 6.99 (AA'BB', 4, aromatic), 6.75, 7.28 (2s, 2, CH-5,8), 9.15 (s, 1, CH=N), and 9.50 (b, 2, 2 OH), $[\alpha]_D$ −88.9°; ORD (*c* 0.746, CH_3OH) $[\Phi]_{700}$ −304°, $[\Phi]_{589}$ −430°, $[\Phi]_{410}$ +1100° (pk), $[\Phi]_{348}$ −11,020° (tr), $[\Phi]_{308}$ +7440° (pk), $[\Phi]_{270}$ −5510° (sh), $[\Phi]_{259}$ −23,140° (tr), and $[\Phi]_{230}$ +7710° (pk); CD $[\theta]_{430}$ 0, $[\theta]_{380}$ +5450, $[\theta]_{356}$ 0, $[\theta]_{330}$ −13,820, $[\theta]_{306}$ 0, $[\theta]_{296}$ +3270, $[\theta]_{288}$ 0, $[\theta]_{270}$ −6540 (sh), $[\theta]_{246}$ −32,020, $[\theta]_{234}$ 0, and $[\theta]_{230}$ +14,540.

Anal. Calcd for $C_{17}H_{18}INO_3$ (411.24): C, 49.65; H, 4.41. Found: C, 49.64; H, 4.48.

(−)-4(*S*)-7-Hydroxy-4-(4-hydroxyphenyl)-6-methoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (8).—To a stirred solution of 4.11 g (10 mmol) of **7** in 300 ml of methanol was added 6 g of sodium borohydride over 1 hr. After stirring for 3 hr, the reaction mixture was evaporated and the residue dissolved in water, acidified with 6 *N* hydrochloric acid, neutralized with sodium bicarbonate, and extracted with ethyl acetate. The organic extract was evaporated and the residue crystallized from ether to afford 2.3 g (81%) of **8**: mp 216–217°; uv max 225 mμ (ε 16,400) (sh), 282 (4800), and 293 (3000) (sh); nmr δ 2.27 (s, 3, NCH_3), 3.42 (s, 2, CH_2-1), 3.54 (s, 3, OCH_3), 3.97 (t, 1, J = 6 Hz, CH-4), 6.28, 6.51 (2 s, 2, CH-5,8), 6.67, 6.97, (AA'BB', 4, aromatic), and 8.97 (b, 2, OH); mass spectrum *m/e* (rel intensity) 285 (29), 242 (100), 241 (87), 227 (25), 225 (65), 211 (55), 210 (37), 199 (12), 197 (14), 182 (17), 181 (32), 169 (13), 165 (15), 153 (18), 152 (19); compound **8** was identical in thin layer chromatographic behavior with natural cherylline[8] in the following solvent systems, acetonitrile–concentrated ammonium hydroxide (90:10), chloroform–methanol (70:30), chloroform–methanol–diethylamine (92:3:5), methanol–acetic acid (1:1); $[\alpha]_D$ −71.9° [lit.[1] $[\alpha]^{25}D$ −69° (*c* 0.2, CH_3OH)]; ORD (*c* 0.249, CH_3OH) $[\Phi]_{700}$ −131°, $[\Phi]_{589}$ −189°, $[\Phi]_{295}$ −12,150° (tr), $[\Phi]_{278}$ +16,040° (pk), $[\Phi]_{258}$ +2520° (tr), $[\Phi]_{242}$ +9170° (pk), and $[\Phi]_{229}$ −13,750° (tr); CD $[\Phi]_{306}$ 0, $[\Phi]_{290}$ −17,570, $[\theta]_{280}$ 0, $[\theta]_{275}$ +3860, $[\theta]_{256}$ +640, $[\theta]_{240}$ +12,860, $[\theta]_{235}$ 0, and $[\theta]_{225}$ −22,290; identical within experimental error, in ORD and CD with natural cherylline.[1]

Anal. Calcd for $C_{17}H_{19}NO_3$ (285.33): C, 71.56; H, 6.71. Found: C, 71.27; H, 6.66.

(+)-4(*R*)-7-Hydroxy-4(4-hydroxyphenyl)-6-methoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (Unnatural Cherylline, Antipode of 8).—This was obtained from **2b** by the methods described for the conversion of **3b** into **8** *via* the dextrorotatory antipodes of **4**, **5**, **6**, and **7**: mp 214–215° (from ether); identical in tlc, uv, and nmr with **8**; ORD and CD mirror images of **8**.

Anal. Calcd for $C_{17}H_{19}NO_3$ (285.33): C, 71.56; H, 6.71. Found: C, 71.63; H, 6.76.

Registry No.—**2a**, 25528-07-8; **2b**, 25528-08-9; **3a**, 25528-09-0; **3b**, 25515-38-2; **4**, 25641-45-6; **5**, 25515-39-3; **6**, 25515-40-6; **7**, 25515-41-7; (−)-(*S*)-**8**, 23367-61-5; (+)-(*R*)-**8**, 25515-34-8.

Acknowledgment.—We are indebted to our Physical Chemistry Department, under the direction of Dr. P. Bommer, for the analytical and spectral data. We are particularly grateful to Dr. V. Toome for the ORD and CD determinations and to Mr. J. O'Brien for technical assistance.

A New Ylide from Tetrakis(trifluoromethyl)cyclopentadienone and Triphenylphosphine

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The reaction between hexafluorobut-2-yne and chlorobis(carbonyl)rhodium dimer gives good yields of tetrakis(trifluoromethyl)cyclopentadienone.[1] When

(1) R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 2699 (1964).