oxide **6** as a mixture of two diastereoisomers from which the major isomer was obtained in a pure crystalline form (67%).

Heating the sulfoxide **6** in benzene at 60 °C for 24 h afforded the 2-oxoazetidine-4-sulfenic acid **3**: 79%; mp 170–172 °C; $[\alpha]^{26}_D$ −118.3° (*c* 0.4, $CHCl_3$). The structure of this compound was determined by its spectral data and elemental microanalysis and then corroborated by converting it quantitatively to the sulfoxide **6** by treating it with methyl acrylate either for 10 min at 60 °C or for 2 h at ambient temperature.

The sulfenic acid **3** is remarkably stable: no decomposition was detected after storage for more than 6 months at 0 °C or after being heated in benzene at 80 °C for 24 h. However, it decomposed upon being heated in xylene at 130 °C. The high stability of this particular sulfenic acid seems to derive from steric hindrance due to the bulky *tert*-butyldimethylsilyl group which prevents its self-condensation into the thiosulfinate **8**.

Experimental Section

NMR data were determined on an 80-MHz Varian FT-80A or a 90-MHz Bruker FT-HFX-10 spectrometer. For other general experimental details see ref 10.

(3*R*,4*R*)-4-[[2-(Methoxycarbonyl)ethyl]thio]-3-phthalimido-2-azetidinone (10). To an ice-cold mixture of the (*R*)- and the (*S*)-sulfoxides **5** (160 mg, 0.5 mmol, 2:1 ratio, respectively)[10] and NaI (200 mg, 1.3 mmol) in acetone (2.5 mL) was added a solution of trifluoroacetic anhydride (0.3 mL, 2.2 mmol) in acetone (6 mL) dropwise during 30 min. To the residue obtained after evaporation was added water (20 mL), and the product was extracted with chloroform, washed with a 1 N solution of sodium thiosulfate (15 mL) and with brine, dried, and evaporated to give the sulfide **10**: 150 mg (98%); mp 126–128 °C (after trituration with ether); IR ($CHCl_3$) 3420, 1790, 1775, 1740 (sh), 1730 cm^{-1}; NMR (80 MHz, $CDCl_3$) δ 2.72 (m, $SCH_2CH_2CO_2$), 3.61 (s, OMe), 5.15 (d, *J* = 4.7 Hz, 4-H), 5.63 (dd, *J* = 4.7, 1.0 Hz, 3-H), 6.53 (br, NH), 7.83 (m, Phth); high-resolution mass spectrum, calcd for $C_{15}H_{14}N_2O_5S$ *m/e* 334.0623, found *m/e* 334.0626; *m/e* 334 (M^+), 291 (M^+ − NH=C=O), 247 (M^+ − $SCH_2CH_2CO_2CH_3$), 187 (PhthCH=C=O^+).

(3*R*,4*R*)-1-(*tert*-Butyldimethylsilyl)-4-[[2-(methoxycarbonyl)ethyl]thio]-3-phthalimido-2-azetidinone (11). To a solution of the sulfide **10** (1.5 g, 4.5 mmol) in DMF (20 mL) were added *tert*-butyldimethylsilyl chloride (800 mg, 5.3 mmol) and triethylamine (2 mL, 14.5 mmol). After being stirred for 15 min at room temperature, the reaction mixture was poured into benzene–ethyl acetate (1:1, 150 mL) and washed with water and with brine. The organic solution was dried, and the residue obtained after evaporation was chromatographed on a short silica gel column (toluene–ethyl acetate, 3:1) to give the title compound **11**: 1.8 g (90%); mp 98–99 °C (from benzene–hexane); $[\alpha]^{26}_D$ −90.0° (*c* 0.9, $CHCl_3$); IR ($CHCl_3$) 1785, 1755, 1730 cm^{-1}; NMR (80 MHz, $CDCl_3$) δ 0.35 and 0.36 (2 s, $SiMe_2$), 1.06 (s, *t*-Bu), 2.59 (m, $SCH_2CH_2CO_2$), 3.51 (s, OMe), 4.94 (d, *J* = 4.9 Hz, azetidine H), 5.63 (d, *J* = 4.9 Hz, azetidine H), 7.82 (m, Phth); high-resolution mass spectrum, calcd for $C_{21}H_{28}SiN_2O_5S$ *m/e* 448.1487, found *m/e* 448.1517; *m/e* 448 (M^+), 391 (M^+ − C_4H_9), 361 (M^+ − $CH_2CH_2CO_2CH_3$), 329 (M^+ − $SCH_2CH_2CO_2CH_3$), 291 (M^+ − *t*-Bu(Me_2)SiN=C=O).

(3*R*,4*R*)-1-(*tert*-Butyldimethylsilyl)-4-[[2-(methoxycarbonyl)ethyl]sulfinyl]-3-phthalimido-2-azetidinone (6). To a stirred solution of the sulfide **11** (1.25 g, 2.8 mmol) in CH_2Cl_2 (100 mL) at −40 °C was added a solution of *m*-chloroperbenzoic acid (500 mg, 87%, 2.5 mmol) in CH_2Cl_2 (100 mL) during 90 min. The solution was washed with aqueous $NaHCO_3$, water, and with brine, dried, and evaporated. The residue contained two isomers of the sulfoxide **6** (TLC and NMR). The reaction mixture was unstable on a silica gel plate. The major isomer of **6** was isolated by crystallization from benzene–hexane: 870 mg (67%); mp 136–138 °C; IR ($CHCl_3$) 1785 (sh), 1770, 1730 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 0.37 and 0.41 (2 s, Me_2Si), 1.08 (s, *t*-Bu), 2.7–2.8 (m, $S(O)CH_2CH_2CO_2$), 3.67 (s, OMe), 4.67 (d, *J* = 5.3 Hz, azetidine H), 5.81 (d, *J* = 5.3 Hz, azetidine H), 7.79 (m, Phth). Anal. Calcd for $C_{21}H_{28}N_2O_6SSi$: C, 54.29; H, 6.07; N, 6.03. Found: C, 54.03; H, 5.88; N, 6.12.

The mother liquor contained a mixture of the two isomeric sulfoxides. For minor isomer of **6** (ca. 20%): NMR δ 1.12 (s, *t*-Bu), 3.38 (s, OMe), 4.77 (d, *J* = 5.3 Hz, azetidine H), 5.68 (d, *J* = 5.3 Hz, azetidine H).

(3*R*,4*R*)-1-(*tert*-Butyldimethylsilyl)-3-phthalimido-2-oxoazetidine-4-sulfenic Acid (3). The sulfoxide **6** (100 mg, 0.2 mmol, major isomer) was heated in benzene (25 mL) at 60 °C for 24 h. The solvent was evaporated, and the residue was crystallized (from benzene–hexane) to give the sulfenic acid **3**: 64 mg (79%); small colorless crystals; mp 170–172 °C dec; $[\alpha]^{26}_D$ −118.3° (*c* 0.4, $CHCl_3$); IR (KBr) 3250 (br), 1785 (sh), 1730 cm^{-1}; NMR (80 MHz, $CDCl_3$) δ 0.39 and 0.43 (2 s, $SiMe_2$), 1.05 (s, *t*-Bu), 4.55 (br s, SOH), 5.20 (d, *J* = 5.3 Hz, azetidine H), 5.81 (d, *J* = 5.3 Hz, azetidine H), 7.83 (m, Phth); high-resolution mass spectrum, calcd for $C_{17}H_{22}N_2O_4SSi$ *m/e* 378.1069, found *m/e* 378.1070; *m/e* 378 (M^+), 361 (M^+ − OH), 329 (M^+ − SOH), 321 (M^+ − C_4H_9), 221 (m^+ − *t*-BuMe$_2$SiN=C=O), 203 (PhthCH=C=S^+), 187 (PhthCH=C=O^+). Anal. Calcd for $C_{17}H_{22}N_2O_4SSi$: C, 53.94; H, 5.86; N, 7.40; S, 8.47. Found: C, 54.20; H, 6.01; N, 7.28; S, 8.75.

Reaction of the Sulfenic Acid 3 with Methyl Acrylate. A solution of the sulfenic acid **3** (20 mg, 0.059 mmol) in methyl acrylate (1 mL) was heated at 60 °C for 10 min. The solvent was evaporated to afford the sulfoxide **6** (quantitative, 2:1 mixture of two isomers). A similar result was obtained when the reaction was performed at ambient temperature for 2 h.

Colorflammine and Berbacolorflammine, Two New Orange-Colored Bis[benzylisoquinoline] Alkaloids from *Pycnarrhena longifolia*

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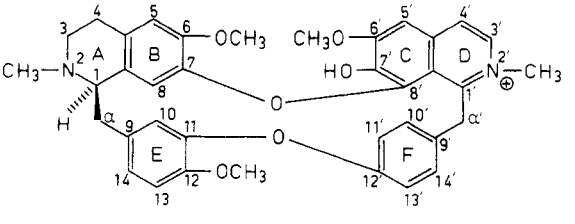
In continuation of our research on Indonesian medicinal plants we studied the alkaloids from a chloroform fraction of *Pycnarrhena longifolia*. In a previous communication the identification of some tertiary bis[benzylisoquinoline] alkaloids, i.e., obaberine, homoaromaline, limacine, aromoline, krukovine, and daphnoline, in a toluene fraction and of some quaternary alkaloids, i.e., magnoflorine and pycnarrhine, in an aqueous fraction were described.[1]

Besides the tertiary alkaloids already found in the toluene fraction, two orange-colored alkaloids were typical for the chloroform fraction. This report describes the isolation and structure elucidation of these two new bis[benzylisoquinoline] alkaloids.

In neutral methanol colorflammine **1** showed UV ab-



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sorption maxima at 439, 333, 292, and 233 nm. Basification did not give shifts and acidification with dilute hydrochloric acid led to a colorless solution with UV maxima at

(1) J. Siwon, R. Verpoorte, T. A. van Beek, H. Meerburg, and A. Baerheim Svendsen, *Phytochemistry*, **20**, 323 (1981).

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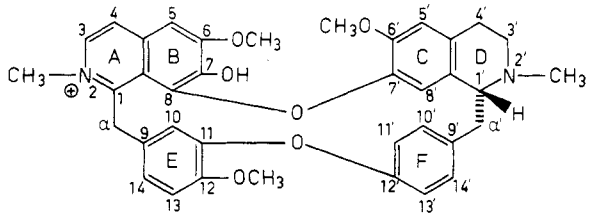
374, 326, 267, and 244 nm. A similar behavior was observed for the alkaloid pycnarrhine.[1] In the mass spectrum no molecular ion was found at either 70 or 12 eV. Reduction with sodium borohydride in ethanol for 2 h yielded one colorless compound. By means of MS, ^{1}H NMR, UV, $[\alpha]^{20}_D$, and TLC comparison with a reference compound this alkaloid was identified as limacusine **3**. To measure the degree of extra unsaturation, we repeated the reduction with sodium borodeuteride in deuterated ethanol. The deuterated alkaloid gave a molecular ion at m/e 611. This means two additional double bounds, one being a carbon–nitrogen double bond. This was further confirmed by means of field-desorption mass spectrometry, which gave a molecular ion at m/e 605 for colorflammine. Also from the ^{1}H NMR the presence of a quaternary nitrogen could be concluded, and three proton singlets were observed at 4.08, 4.01, 3.86, 3.86, and 2.45 ppm, which were explained as three methoxy groups and one quaternary *N*-methyl and one tertiary *N*-methyl group.



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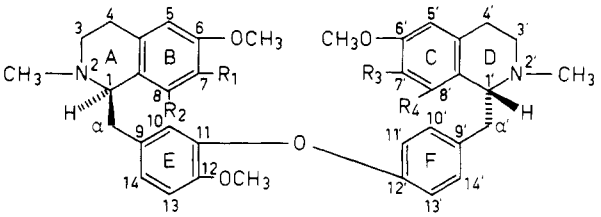

3, $R_1 + R_4 = -O-$; $R_2 = H$; $R_3 = OH$

4, $R_1 = OH$; $R_2 + R_3 = -O-$; $R_4 = H$

To establish the sites of the two double bonds, we made a detailed 250-MHz ^{1}H NMR study of limacusine **3** and the alkaloid obtained by reduction with $NaBD_4$. In the trideuterio compound the signals due to the four benzylic hydrogens were observed at 3.12 + 2.50 (α-1 + α-2) and at 3.40 + 2.82 ppm (α'-1 + α'-2), leaving only ring A and D for the double bonds. The disappearance of three signals (60.6, 44.2, and 22.6 ppm) in the ^{13}C NMR spectrum, corresponding with carbons C-1, C-3, C-4 or C-1′, C-3′, C-4′ of the trideuterio alkaloid mass spectrum and a 3-mass-unit difference for the 381 fragment of limacusine and the corresponding fragment of the trideuterio compound[2] gave further evidence for this conclusion. From homonuclear decoupling and NOE difference experiments it was concluded that the H-1′ signal has a shift of 4.36 ppm. This signal was not observed in the trideuterio compound. From this it was concluded that colorflammine has an unsaturated D ring (structure **1**). The stereochemistry of C-1 is the same as for limacusine, e.g., an *R* configuration, which is in accordance with the positive [α] found for colorflammine (e.g., compare with hypoepistephanine, which has a similar [*R*, −] configuration and $[\alpha]_D$ +183.8°, and epicoclobine, which has a [−, *R*] configuration and $[\alpha]_D$ −123°).[3]

For berbacolorflammine the following facts are of importance: the UV spectrum, FD mass spectrum, and polarity are similar to those of colorflammine. Reduced berbacolorflammine has identical UV, MS, ^{1}H NMR, $[\alpha]^{20}_D$, and TLC behavior as limacine **4**. The mass spectrum of berbacolorflammine reduced with $NaBD_4$ showed the following important signals: m/e 611, 490, 384, 192; so here two additional double bonds are also present in the A or D ring.[2]

The 2.57-ppm NCH_3 signal corresponds to $N_2'CH_3$ (at 2.60 ppm in limacine). The other NCH_3 group is shifted to a lower field from which it is concluded that the double bonds are situated in the A ring. Therefore, berbacolorflammine has structure **2**. Additional evidence for the fact that the double bonds are situated in the A ring is obtained from comparison of the ^{13}C NMR spectra of berbacolorflammine and limacine: the signals of C-4′ (25.6 ppm) and C-1′ (63.8 ppm) in limacine are also present in berbacolorflammine (25.6 and 63.9 ppm) but not the C-4 and C-1 signals (21.8 and 61.4 ppm).

Experimental Section

Extraction. The extraction of the plant material and the preparation of the chloroform fraction are described in a previous publication.[1]

Apparatus. UV spectra were recorded in MeOH. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL PS-100 apparatus or on a Bruker WM 250 instrument, both in the Fourier transform mode in $CDCl_3$. Shifts are presented in δ values relative to Me_4Si. Mass spectra were obtained with an AEI MS 902 spectrometer using a direct inlet system and an ionization energy of 70 eV or with a Varian MAT 711 spectrometer equipped with a combined EI/FD source, using the field-desorption mode.

$[\alpha]^{20}_D$ was recorded in $CHCl_3$. IR spectra were recorded in KBr.

TLC. For the separation and identification of the alkaloids the following TLC systems were used: S1, MeOH–H_2O–concentrated NH_4OH (8:1:1); S2, $CHCl_3$–MeOH–concentrated NH_4OH (14:5:1); S3, $CHCl_3$–cyclohexane–Et_2NH (10:8:3); S4, toluene–EtOAc–Et_2NH (7:2:1); S5, hexane–MeCOEt–Et_2NH (10:8:3); S6, EtOAc–*i*-PrOH–concentrated NH_4OH (9:7:1). All solvent system were used in combination with ready-made plates (Si 60 F 254, Merck) in saturated chromatography chambers. Detection of alkaloids was made with UV light (254 and 366 nm) and iodoplatinate reagent.

Separation of the Alkaloids. The chloroform fraction was first separated on a Merck Lobar Si 60 column (size C) with S1 as eluant. The orange-colored fraction was collected. This fraction was then separated by means of preparative TLC (silica) with solvent S2 in two orange-colored bands with R_f 0.48 and 0.44, respectively. The band with R_f 0.48 gave 50 mg of pure colorflammine and the band with R_f 0.44 gave 15 mg of pure berbacolorflammine.

Characterization of the Alkaloids. Colorflammine: TLC, R_f in S2 0.48; strong reaction with iodoplatinate reagent, extinction in UV 254 nm, and orange fluorescence in UV 366 nm; UV λ_{max} 233 nm, 292, 333, 439 (neutral) 244, 267, 326, 374 (acid). IR λ_{max} 3410, 2910, 1492 cm^{-1}: FD mass spectrum, m/e 605; optical rotation $[\alpha]^{20}_D$ +1050° (*c* 0.06); ^{1}H NMR (100 MHz) δ 2.45 (3 H, s), 3.86 (6 H, s), 4.01 (3 H, s), 4.08 (3 H, s), 4.34 (1 H, br s), 4.74 (1 H, s), 5.92 (1 H, s), 6.04–7.71 (aromatic); ^{13}C NMR (63 MHz) δ 25.1 (t, C_4), 35.9 (t), 37.6 (t), 42.0 (q, NCH_3), 46.2 (q, $N'CH_3$), 47.5 (t, C_4), 55.5 (q, OCH_3), 55.8 (q, OCH_3), 56.0 (q, OCH_3), 62.6 (d, C_1), 102.3 (d), 110.7 (d), 111.1 (d), 112.0 (d), 116.1 (d), 120.0 (s), 122.2 (d), 122.9 (d), 123.6 (d), 123.6 (d), 124.1 (s), 126.2 (d), 126.2 (s), 129.4 (s), 129.6 (s), 130.6 (d), 131.2 (d), 132.6 (s), 134.5 (s), 143.4 (s), 146.5 (s), 147.3 (s), 148.7 (s), 149.1 (s), 153.3 (s), 153.7 (s), 161.6 (s, C_1').

(2) M. Hesse, H. O. Bernard, "Progress in Mass Spectrometry", Verlag Chemie, Weinheim/Bergstr., Germany, 1975, Vol. 3, p 74.

(3) K. P. Guha, B. Mukherjee, and R. Mukherjee, *J. Nat. Prod.* **42**, 1 (1979).

Reduction of Colorflammine. Four milligrams of colorflammine was dissolved in 2.5 mL of ethanol and 0.5 mL of H_2O, and the mixture was stirred for 2 h with addition of 10 mg of $NaBH_4$. The alcohol was evaporated by blowing N_2 over the solution, and then the residue was extracted 3 times with ether. The ether was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. A white amorphous residue remained (trihydro derivative). This was repeated with $NaBD_4$, C_2H_5OD, and D_2O (trideuterio derivative).

Trihydro Derivative. The trihydro derivative had the same R_f values in systems S3–S6 as limacusine. The other possible diastereoisomer (homoaromoline) could not be observed on TLC in the reaction product. UV λ_{max} 281 nm; mass spectrum, (230 °C), *m/e* 609 (6.3), 608 (M^+, 16.8), 607 (8.4), 501 (0.5), 381 (8.9), 228 (15.8), 198 (8.4), 193 (21), 192 (100), 191.5 (6.3), 191 (36.8), 190 (31.6); exact mass calcd for $C_{37}H_{40}N_2O_6$ 608.2894, found 608.2884; ^1H NMR (250 MHz) δ 2.50 (dd, $H_{\alpha\text{-}2}$), 2.50–2.90 (m, 5 H), 2.55 (s, NCH_3), 2.57 (s, $N'CH_3$), 2.82 (dd, $H_{\alpha'\text{-}2}$), 2.90–3.06 (m, 2 H), 3.12 (d, $H_{\alpha\text{-}1}$), 3.40 (d, $H_{\alpha\text{-}1'}$), 3.42 (s, 6-OCH_3), 3.59 (d, H_1), 3.45–3.52 (m, 1 H), 3.78 (s, 6'-OCH_3), 3.95 (s, 12-OCH_3), 4.36 (d, H'_1), 5.2–5.4 (br s, OH), 6.38 s, $H_{5'}$), 6.41 (s, H_8), 6.45 (s, H_5), 6.57 (s, H_{10}), 6.83 (br s, $H_{13'}$ and $H_{14'}$), 6.92 (d, H_{14}), 6.96 (d, H_{13}), 7.10 (d, $H_{12'}$), 7.36 (d, $H_{11'}$). **Note:** The shifts and coupling constants of the various protons (an exception are the methoxy protons) are extremely sensitive to temperature changes and traces of acid or base, even in $CDCl_3$. Shift variations of 0.15 ppm for some protons under apparently the same conditions were observed. Future workers who want to compare their data with the ones presented here should bear this in mind. ^{13}C NMR (only aliphatic carbons; 63 MHz) δ 22.6, 26.4, 40.1, 41.1, 42.2, 43.2, 44.2, 46.5, 55.5, 56.1, 56.4, 60.6, 65.4; optical rotation $[\alpha]^{20}_D$ +70° (*c* 0.03).

Trideuterio Derivative. UV spectrum and TLC behavior were the same as for the trihydro derivative. Mass spectrum (230 °C), *m/e* (relative intensity) 611 (18), 610 (9), 504 (0.6), 384 (12), 228 (12), 207 (56), 194 (13), 193 (52), 192.5 (20), 191 (18), 190 (15); exact mass calcd for $C_{37}H_{37}D_3N_2O_6$ 611.3074, found 611.3074; ^1H NMR (250 MHz), similar to that of the trihydro derivative except that the proton at 4.36 ppm and two protons from the multiplet between 2.50 and 2.90 ppm have vanished and that the doublet of doublets at 2.82 ppm has become a doublet; ^{13}C NMR (63 MHz), similar to that of the trihydro derivative except for the signals at 22.6, 44.2, and 60.6 ppm, which have vanished.

Limacusine. UV, ^1H NMR, and mass spectra were the same as for the trihydro derivative.

Berbacolorflammine: TLC, R_f in S_2 0.44; strong reaction with iodoplatinate reagent, extinction in UV 254 nm, and orange fluorescence in UV 366 nm; UV (MeOH) λ_{max} 445 nm, 338, 294, 234; UV (MeOH + HCl) λ_{max} 372 nm, 323, 275, 268, 228; FD mass spectrum, *m/e* 605; ^1H NMR (100 MHz) δ 2.57 (s, 3 H), 3.53 (s, 3 H), 3.85 (s, 3 H), 3.90 (s, 6 H), 4.08 (br s, 1 H), 5.65 (s, 1 H), 6.10–7.52 (aromatic); ^{13}C NMR (25.2 MHz) δ 25.6 (t, $C_{4'}$), 35.4 (t), 35.8 (t), 42.3 (q, N'Me), 45.6 (t, $C_{3'}$), 46.2 (q, NMe), 55.9 (q, OCH_3), 56.2 (q, OCH_3), 56.2 (q, OCH_3), 63.9 (d, $C_{1'}$), 100.8 (d), 112.1 (d), 112.2 (d), 119.4 (d), 119.4 (s), 121.4 (d), 121.5 (d), 123.0 (s), 123.1 (d), 127.0 (s), 127.4 (s), 128.3 (s), 129.7 (d), 129.8 (s), 132.0 (d), 135.0 (s), 138.5 (s), 143.4 (s), 148.3 (s), 148.6 (s), 149.0 (s), 150.0 (s), 155.5 (s), 162.5 (s); optical rotation $[\alpha]^{20}_D$ 1000° (*c* 0.004). Reduction of berbacolorflammine was carried out in the same way as described for colorflammine.

Trihydro Derivative. The trihydro derivative had the same R_f values in systems S_3–S_6 as limacine. The other possible diastereoisomer (thalrugosine) could not be observed on TLC in the reaction product. UV λ_{max} 284 nm; mass spectrum (220 °C), *m/e* (relative intensity) 609 (18), 608 (M^+, 45), 607 (23), 593 (4), 471 (0.5), 381 (27), 367 (9), 198 (8), 193 (18), 192 (100), 191.5 (18), 191 (95), 190 (77); exact mass calcd for $C_{37}H_{40}N_2O_6$ 608.2870, found 608.2886; ^1H NMR δ 2.36 (s, NCH_3), 2.66 (s, $N'CH_3$), 3.37 (s, 6'-OCH_3), 3.78 (s, 6-OCH_3), 3.93 (s, 12-OCH_3), 6.05–7.32 (m, aromatic); optical rotation $[\alpha]^{20}_D$ −205° (*c* 0.008).

Trideuterio Derivative. TLC, the trideuterio derivative had the same R_f values in systems S_3–S_6 as limacine; mass spectrum (230 °C), *m/e* (relative intensity) 612 (8), 611 (M^+, 16), 610 (6), 596 (1.5), 474 (0.1), 384 (13), 370 (3), 198 (11), 193 (52), 192.5 (22), 192 (100), 191 (27), 190 (26).

Limacine (aliphatic carbons only): UV, ^1H NMR, and mass spectra were the same as for the trihydro derivative; ^{13}C NMR (25.2 MHz) δ 21.8 (C-4), 25.6 (C-4'), 37.9 (C-α'), 42.0 (C-α), 42.3 (NMe), 42.7 (NMe'), 44.2 (C-3), 45.4 (C-3'), 56.1 (OCH_3), 56.1 (OCH_3), 56.2 (OCH_3), 61.4 (C-1), 63.8 (C-1').

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Catalytic Conversion of Alcohols. Origin of Anti-Saytzeff Dehydration[1]

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Recently Floris reported what was believed to be the first example of an anti-Saytzeff orientation (1-alkene formation from 2-alkanols) for the dehydration of an alcohol with an alumina catalyst.[2a] Chen and Elofson[2b] attributed the selectivity observed by Floris to the stereochemical effect due to hydrogen bonding of the hydroxyl hydrogen to the iron atom of the ferrocenyl group of the 2-ferrocenyl-3-methyl-2-butanol (II) rather than a specific catalytic effect. However, Kieboom[3] pointed out that anti-Saytzeff orientation is generally observed in acid-catalyzed dehydration of substituted 2-phenyl-3-methyl-2-butanols (III); presumably steric repulsion in the transition state resulting from interaction of the 3-methyl group with the 2-hydrogen atom of the benzene ring is responsible for the unusual alkene distribution.[3,4] Kieboom predicted that the isomeric tertiary alcohols CCR(OH)C(C)C (I) would show anti-Saytzeff orientation for any bulky R substituent.

Pines had reported, prior to Floris' publication, an anti-Saytzeff preference for the dehydration of 2,3-dimethyl-2-butanol (V) with alumina;[5] we have confirmed the anti-Saytzeff nature of this elimination. We also obtained similar results for the dehydration of 2,3-dimethyl-2-pentanol (IV) with alumina. Thus, with an alumina catalyst, R = methyl is as effective as R = ferrocenyl in promoting formation of the anti-Saytzeff product.

The anti-Saytzeff product predominates (80–91%, Table I) in the dehydration of 2-aryl-3-methyl-2-butanols (III), using a sulfuric acid catalyst in acetic acid solvent. However, when we used Kieboom's procedure to dehydrate V at room temperature with the sulfuric acid in acetic acid, an equilibrium alkene mixture containing only about 10% of the terminal alkene was obtained. This was the result, even at very low conversions. Thus, with 10% sulfuric acid

(1) Based on experimental work done at Potomac State College, Keyser, WV.
(2) (a) Floris, B. *J. Org. Chem.* **1976**, *41*, 2774. (b) Chen, S. C.; Elofson, R. M. *Chem. Ind.* **1978**, 64.
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