the molecular ion, but a peak (1.5%) at *m/e* 279.1231 (calcd for $C_{20}H_{26}O_6$, C_5H_7O, 279.1243). Other significant peaks were at *m/e* (composition, %) 263 ($M^+ - C_5H_7O_2$, 22.8), 262 ($M^+ - C_5H_8O_2$, 26.8), 245 ($M^+ - C_5H_7O_2 - H_2O$, 3.4), 244 ($M^+ - C_5H_8O_2 - H_2O$, 49.6), 229 ($M^+ - C_5H_8O_2 - H_2O - CH_3$, 6.3), 100 ($C_5H_8O_2$, base peak), and 99 ($C_5H_7O_2$, 31.3).

X-Ray Analysis of Eufoliatorin. Intensity data were measured on a Hilger-Watts diffractometer (Ni filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). A crystal measuring approximately 0.15 × 0.4 × 0.5 mm was used for data collection; no absorption correction was made (μ = 8.4 cm^{-1}). A total of 2210 reflections were measured for $\theta < 76°$, of which 1992 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure[22] and was refined by full-matrix least squares. In the final refinement anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.055$ and $wR = 0.076$ for the 1992 observed reflections. The final difference map has no peaks greater than ±0.3 e $Å^{-3}$.

Acknowledgment. We wish to thank Mr. R. C. Rosanske for help with determination of the ^{13}C NMR spectra and the nuclear Overhauser effects.

Registry No.—**1a,** 62197-54-0; **1b,** 62197-55-1; **1c,** 62197-56-2; **1d,** 62197-57-3; **2,** 62197-58-4; **3,** 62197-59-5; **4a,** 62197-60-8; **4b,** 62197-61-9; **4c,** 62197-64-2; **5a,** 62197-62-0; **5b,** 62197-63-1; **6,** 62197-65-3.

Supplementary Material Available. Tables IV, V, and VI listing bond distances, bond angles, and torsion angles of compound **6** (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This article is dedicated to the memory of S. Morris Kupchan, a long-time friend who published several noteworthy papers on constituents of *Eupatorium* species in the decade before his untimely death in 1976.
(2) Work at Florida State University supported in part by USPH Grant CA-13121 through the National Cancer Institute.
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(6) For references to earlier work, on *Eupatorium* species, see ref 3, which also includes citations concerning the flavonoids of *E. perfoliatum* and related species.
(7) The crude extract as a whole was rather polar and difficult to separate. The four substances we were successful in purifying represented a relatively small portion of the total extract.
(8) W. Herz and R. P. Sharma, *J. Org. Chem.*, **41,** 1248 (1976).
(9) See ref 3 for reasons governing choice of this reagent combination.
(10) Use of paramagnetic shift methods which can occasionally be used to solve this vexing problem was ineffective in this case and that of the other substances described in this report because of line broadening, overlapping of signals, etc. The applicability of the solvent shift method of C. R. Narayanan and N. K. Venkatasubramaniam [*Tetrahedron Lett.*, 5865 (1966); *J. Org. Chem.*, **33,** 3156 (1968)], which gives good results with 11,13-dihydroeudesmanolides, to 11,13-dihydrogermacranolides and 11,13-dihydroguaianolides of known stereochemistry is currently being tested.
(11) For leading citations, see ref 8.
(12) See, for example, (a) N. S. Bhacca and N. H. Fischer, *Chem. Commun.*, 68 (1969); (b) F. Sorm, M. Suchý, M. Holub, A. Linek, I. Hadinec, and C. Novák, *Tetrahedron Lett.*, 1893 (1970); (c) S. K. Talapatra, A. Patra, and B. Talapatra, *Chem. Commun.*, 1534 (1970); (d) E. J. Gabe, S. Neidle, D. Rogers, and C. E. Nordman, *ibid.*, 559 (1971); (e) K. Tori, I. Horibe, Y. Tamura, and H. Tada, *J. Chem. Soc., Chem. Commun.*, 620 (1973); (f) M. A. Irwin and T. A. Geissman, *Phytochemistry,* **12,** 875 (1973); (g) R. W. Doskotch, S. L. Keely, and C. D. Hufford, *J. Chem. Soc., Chem. Commun.*, 1137 (1972); (h) A. T. McPhail and K. D. Onan, *J. Chem. Soc., Perkin Trans. 2,* 1798 (1975); (i) K. Tori, I. Horibe, Y. Tamura, K. Kuriyama, H. Tada, and K. Takeda, *Tetrahedron Lett.*, 387 (1976); (j) A. Quick and D. Rogers, *J. Chem. Soc., Perkin Trans. 2,* 465 (1976).
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Grisabine and Grisabutine, New Bisbenzylisoquinoline Alkaloids from *Abuta grisebachii*

Roshan Ahmad and Michael P. Cava*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19174

Received November 15, 1976

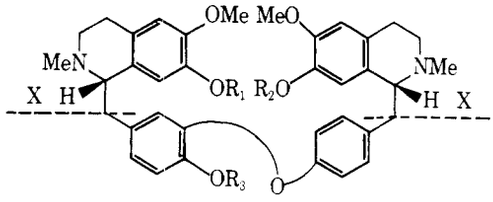
Grisabine and grisabutine, new bisbenzylisoquinoline alkaloids from *Abuta grisebachii,* Triana & Planchon, have been assigned structures **1** and **2,** respectively, on the basis of spectroscopic and chemical evidence.

Recent studies from our laboratory have led to the isolation of a number of new alkaloids from plants of the tropical American genus *Abuta* (Menispermaceae).[1] We now wish to report the isolation and structure determination of two new bisbenzylisoquinoline alkaloids, grisabine (**1**) and grisabutine (**2**), from the Amazonian species *Abuta grisebachii.*[2]

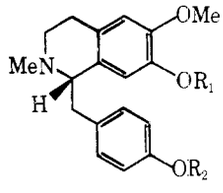
Grisabine (**1**) was obtained as white needles, mp 148–149 °C. The composition $C_{37}H_{42}N_2O_6$ was determined by high-resolution mass spectrometry.

The infrared spectrum (KBr) of grisabine showed a band at 3400 cm^{-1}, attributable to a nonassociated phenolic group. The NMR spectrum of grisabine showed the presence of three superimposed aromatic methoxyls at δ 3.83, two nonequivalent methylimino groups at δ 2.43 and 2.48, and a band of 11 unresolved aromatic protons in the range of δ 6.38–7.01.

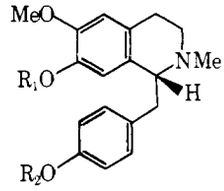
The mass spectrum of grisabine is typical of that of a bisbenzylisoquinoline alkaloid containing only a single tail-to-tail ether bridge. Thus, the molecular ion at *m/e* 610 was quite weak (4%), while the two identical head fragments **13** formed the base peak at *m/e* 192.



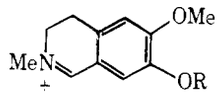
1, $R_1 = R_2 = H$; $R_3 = Me$
2, $R_1 = R_2 = R_3 = H$
3, $R_1 = R_2 = R_3 = Me$
4, $R_1 = R_2 = CD_3$; $R_3 = Me$
5, $R_1 = R_2 = R_3 = CD_3$



6, $R_1 = R_2 = Me$
7, $R_1 = CD_3$; $R_2 = Me$
8, $R_1 = R_2 = CD_3$



9, $R_1 = Me$; $R_2 = H$
10, $R_1 = CD_3$; $R_2 = H$
11, $R_1 = CD_3$; $R_2 = Me$
12, $R_1 = R_2 = CD_3$



13, R = H
14, R = Me
15, R = CD_3

The ultraviolet absorption band of grisabine at 287 nm underwent a bathochromic shift to 305 nm, indicative of the presence of phenolic functionality. The presence of two phenolic functions in grisabine was revealed by its reaction with excess diazomethane, which afforded the amorphous *O,O*-dimethylgrisabine (**3**). The composition $C_{39}H_{46}N_2O_6$ was determined by high-resolution mass spectrometry. The NMR spectrum of **3** showed the presence of three resolved methoxyls at δ 3.59, 3.62, and 3.77 and two superimposed methoxyls at δ 3.80; of the 11 aromatic protons of **3**, two were resolved as singlets at δ 6.10 and 6.16 (H-8 and H-8′) and two as singlets at δ 6.56 and 6.57 (H-5 and H-5′).

The corresponding reaction of grisabine with diazomethane-d_2 in dioxane–deuterium oxide yielded the corresponding *O,O*-bistrideuteriomethyl derivative (**4**). A comparison of the NMR spectra of **3** and **4** clearly indicated that the two methoxyls introduced into grisabine in **3** are represented by the signals at δ 3.59 and 3.62. The mass spectra of **3** and **4** show base peaks at *m/e* 206 (**14**) and 209 (**15**), respectively, confirming the presence of a phenolic hydroxyl in each of the head units of grisabine.

The structure and stereochemistry of *O,O*-dimethylgrisabine (**3**) were established chemically by treatment of **3** with sodium in liquid ammonia, which cleanly cleaved the molecule into phenolic and nonphenolic portions. The nonphenolic product was identical with authentic (*S*)-*O*-methylarmepavine (**6**), while the phenolic product was identical with authentic (*R*)-armepavine (**9**).

The location of the phenolic functions of grisabine in the isoquinoline units was shown by sodium–ammonia cleavage of its bistrideuteriomethyl ether **4**, which afforded the fragments (*S*)-7-*O*-trideuteriomethyl-12-*O*-methyl-*N*-methylcoclaurine (**7**) and (*R*)-7-trideuteriomethyl-*N*-methylcoclaurine (**10**). The structure of **10** was confirmed by deuteriomethylation to give (*R*)-*O,O*-bis(trideuteriomethyl)-*N*-methylcoclaurine (**12**), which was identical with an authentic sample. The structure of **7** was established by reaction of **10** with diazomethane to give the ether **11**, which differed from **7** only in the opposite sign of its rotation.

The above observations establish the structure of grisabine as **1**. It is therefore the *SR* diastereomer of the known alkaloid cuspidaline[3] (**1**, *RR*).

Grisabutine (**2**), mp 192–193 °C, formed white needles from methanol, and had the molecular composition $C_{36}H_{40}N_2O_6$, as shown by mass spectrometry. Its mass spectrum showed a fairly weak (15%) molecular ion at *m/e* 598, the base peak appearing at *m/e* 192, as in the case of grisabine. The methyl region of the NMR spectrum of **2** was remarkably simple, consisting only of two superimposed methoxyls at δ 3.71 and two superimposed methylimino groups at δ 2.32.

Treatment of grisabutine with excess diazomethane afforded an *O*-trimethyl derivative which proved to be identical in all respects with *O*-dimethylgrisabine (**3**). The structure determination of **2** consequently required only a proof of the location of the three phenolic hydroxyl groups.

Deuteriomethylation of grisabutine afforded the tristrideuteriomethyl derivative **5**, which was reductively cleaved by sodium in liquid ammonia. The nonphenolic cleavage product was shown to be (*S*)-*O,O*-bis(trideuteriomethyl)-*N*-methylcoclaurine (**8**) by comparison with an authentic sample; the phenolic product was identical with the phenol **10** derived from the grisabine derivative **4**.

Structure **2** is therefore established for grisabutine, which is the *SR* enantiomer of the known alkaloid berbamunine[4] (**2**, *RS*).

Experimental Section

Melting points are uncorrected. NMR spectra were determined in $CDCl_3$ solution (unless otherwise indicated) with tetramethylsilane as internal standard using a Varian A-60 spectrometer; infrared (KBr), ultraviolet (EtOH solution), mass spectra, and optical rotations were determined using Perkin-Elmer Models 137, 202, 270, and 141 instruments, respectively. All preparative chromatography (PLC) was carried out on silica plates using 10:1 $CHCl_3$–MeOH. *Abuta grisebachii* (*Schunke 5498*) was collected in Loreto, Coronel, Portillo, Peru, and identified by B. A. Krukoff. A voucher specimen has been deposited at the New York Botanical Garden and at other institutions.

Isolation of Grisabine (1) and Grisabutine (2) from *Abuta grisebachii*. Six pounds of ground stems of *Abuta grisebachii* was exhaustively extracted with aqueous ammonia–ether (four times with 6 L of ether). The combined ether extracts on evaporation gave 48 g of crude residue. This was extracted with 2 N HCl, the extract was basified with NH_4OH, and the free bases were taken up in $CHCl_3$. The dried bases obtained after evaporation of the $CHCl_3$ (12 g) were subjected to gradient pH countercurrent distribution between chloroform and aqueous acid, starting with pH 6.5 citrate–phosphate buffer and ending with 3 M phosphoric acid. The acidic aqueous layers were basified, reextracted with chloroform, and combined into several fractions (A–G) on the basis of TLC results.

Fraction D (4.4 g) crystallized from MeOH to give colorless needles (2.9 g) of grisabutine (**2**): mp 192–193 °C; $[\alpha]_D$ −50.0° (*c* 0.5, $CHCl_3$); IR 3400 cm^{-1} (OH); UV λ_{max} (ϵ) 224 nm (17 282), 239 (17 670), 287 (10 131), 320 (sh) (1787); λ_{max} (NaOH) (ϵ) 224 nm (17 345), 242 (17 640), 305 (11 084), 343 (sh) (1311); NMR (Me_2SO-d_6) δ 2.32 (s, 6 H, 2 NMe), 3.71 (s, 6 H, 2 OCH_3); mass spectrum *m/e* (rel intensity) 596 (M^+, 15), 404 (M − X, 13), 192 (X, 100), 175 (6); high-resolution mass spectrum *m/e* 596.28509 ($C_{36}H_{40}N_2O_6$ requires *m/e* 596.28863).

Fraction F (1.78 g) on crystallization from MeOH gave white needles of grisabine (**1**, 1.4 g), mp 145–146 °C. Recrystallization from MeOH raised the melting point to 148–149 °C; $[\alpha]_D$ −60.2° (*c* 0.5, $CHCl_3$); IR 3400 cm^{-1} (OH); UV λ_{max} (ϵ) 224 nm (17 875), 237 (18 250), 287 (15 000); λ_{max} (NaOH) (ϵ) 223 nm (18 300), 237 (19 200), 305 (3721); NMR δ 2.43, 2.48 (s, 3 H each, 2 NMe), 3.83 (s, 9 H, 3 OCH_3); mass spectrum *m/e* (rel intensity) 610 (M^+, 4), 418 (M^+ − X, 4), 192 (X, 100), 175 (15); high-resolution mass spectrum *m/e* 610.30206 ($C_{37}H_{42}N_2O_6$ requires 610.30428).

***O,O,O*-Trimethylgrisabutine (3).** To a solution of **2** in methanol–ether was added ethereal diazomethane and the mixture was set aside in the dark overnight. The usual workup gave **3** as an amorphous solid. Further purification was carried out by PLC: $[\alpha]_D$ −10° (*c* 1.0,

$CHCl_3$); NMR δ 2.47, 2.51 (s, 3 H each, 2 NMe), 3.59, 3.62, 3.77, 3.80 (s, 3 H, 3 H, 3 H, and 6 H, 5 OMe), 6.10, 6.16, 6.56, 6.57 (1 H, each), 6.70–7.11 (m, 7 H); mass spectrum *m/e* (rel intensity) 638 (M^+, 20), 432 ($M^+ - X$, 20), 206 (X, 100), 190 (95); high-resolution mass spectrum *m/e* 638.33637 ($C_{39}H_{46}N_2O_6$ requires 638.33558).

***O,O,O*-Tris(trideuteriomethyl)grisabutine (5).** To a cooled solution of excess diazomethane in dioxane (10 mL) and D_2O (1 mL) was added a solution of **2** (50 mg) in dioxane (2 mL) and D_2O (1 mL). After standing for 24 h in the dark, the usual workup afforded **5** as an amorphous solid (45 mg) which was purified by PLC: NMR δ 2.46, 2.51 (s, 3 H each, 2 NMe), 3.80 (s, 6 H, 2 OMe), 6.11, 6.17 (s, 1 H each), 6.58 (s, 2 H), 6.73–7.15 (m, 7 H).

Sodium–Ammonia Cleavage of 3. To liquid ammonia (500 mL) at −78 °C was added alternatively, with stirring, small pieces of sodium and portions of a solution of **3** (320 mg) in dry THF, allowing the color to remain blue prior to each new addition of the alkaloid solution. Finally, more sodium was added until the blue color persisted for 30 min. The ammonia was allowed to evaporate overnight, and the residue was dissolved in water and extracted with $CHCl_3$ to give the nonphenolic fraction (120 mg). The aqueous layer, after saturation with NH_4Cl (pH 8–9), was extracted with $CHCl_3$ (addition of some $NaBH_4$ retarded air oxidation of the phenolic alkaloids) to give the phenolic fraction (130 mg). Both phenolic and nonphenolic fractions were purified by PLC.

From the nonphenolic fraction, **6** was isolated as an oil: $[\alpha]_D$ +83° (*c* 1.0, MeOH); NMR δ 2.52 (s, 3 H, NMe), 3.56, 3.76, 3.82 (s, 3 H, each, OMe), 6.10 (s, 1 H), 6.59 (s, 1 H), 6.80 (d, 2 H), 7.07 (d, 2 H). The rotation and NMR values were identical with those of (*S*)-*O*-methylarmepavine (**6**) as reported. The oxalate of **6** crystallized from ethanol–ether as white needles, mp 112 °C, $[\alpha]_D$ +99.5° (*c* 0.05, $CHCl_3$). A mixture melting point of the oxalate with an authentic sample gave no depression.

From the phenolic fraction **9** was obtained as an amorphous solid: $[\alpha]_D$ −81.9° (*c* 0.5, MeOH); NMR δ 2.54 (s, 3 H, NMe), 3.52, 3.80 (s, 3 H each, 2 OMe), 6.02 (s, 1 H), 6.60 (s, 1 H), 6.66 (d, 2 H), 6.80 (d, 2 H). The rotation and NMR values were identical with those reported for (*R*)-armepavine (**9**). The oxalate was crystalline (EtOH–ether), mp 207–208 °C, $[\alpha]_D$ −84° (*c* 0.5, MeOH); its mixture melting point with an authentic sample gave no depression.

Sodium–Ammonia Cleavage of 5. The sodium–liquid ammonia cleavage was carried out on **5** (330 mg) exactly as described for **3**, and the products were separated into nonphenolic and phenolic fraction. From the nonphenolic fraction **8** was obtained after PLC purification as an oil (114 mg): NMR δ 2.53 (s, 3 H, NMe), 3.81 (s, 3 H, OMe), 6.01 (s, 1 H), 6.60 (s, 1 H), 6.81 (d, *J* = 9 Hz, 2 H), 7.08 (d, *J* = 9 Hz, 2 H). The oxalate of **8** was crystallized from EtOH–ether: mp 128–129 °C $[\alpha]_D$ +98° (*c* 0.5, $CHCl_3$); mass spectrum *m/e* (rel intensity) 333 (M^+, <1), 332 (1), 209 (100), 124 (13). These values were identical with those reported[1b] for (*S*)-*O,O*-bis(deuteriomethyl)-*N*-methylcoclaurine. A mixture melting point of the oxalate with an authentic sample resulted in no depression.

The phenolic fraction after PLC purification afforded **10** as an oil: NMR δ 2.55 (s, 3 H, NMe), 3.83 (s, 3 H, OMe), 6.01 (s, 1 H), 6.61 (s, 1 H), 6.66 (d, *J* = 9 Hz, 2 H), 6.80 (d, *J* = 9 Hz, 2 H). The oxalate crystallized from EtOH–ether: mp 210–212 °C, $[\alpha]_D$ −95.6° (*c* 0.32, MeOH); mass spectrum *m/e* (rel intensity) 316 (M^+, 12), 285 (80), 209 (100), 194 (10), 191 (15).

Deuteriomethylation of 10. Compound **10** was trideuteriomethylated as described for **2** to give the amorphous **12**, the oxalate of which crystallized from EtOH–ether, mp 130–131 °C, $[\alpha]_D$ −98° (*c* 0.5, $CHCl_3$). The mixture melting point of **12** oxalate with an authentic sample gave no depression; furthermore, the NMR and IR of base **12** were identical with those of its enantiomer **8** (see above).

***O,O*-Dimethylgrisabine (3).** Treatment of **1** with excess of diazomethane and the usual workup afforded **3** which was identical in all respects with the product obtained from the methylation of grisabutine (**2**).

***O,O*-Bis(trideuteriomethyl)grisabine (4).** About 300 mg of grisabine (**1**) was trideuteriomethylated as described for **2** to give, after PLC purification, the amorphous **4** (300 mg): NMR δ 2.48, 2.52 (s, 3 H each, 2 NMe), 3.78 (s, 3 H, OMe), 3.80 (s, 6 H, 2 OMe), 6.10 (s, 1 H), 6.15 (s, 1 H), 6.56 (s, 2 H), 6.73–7.25 (m, 7 H); mass spectrum *m/e* (rel intensity) 644 (M^+, 15), 626 (5), 435 (18), 420 (6), 209 (100), 193 (25).

Sodium–Ammonia Cleavage of 4. The sodium–ammonia cleavage was carried out on **4** (275 mg) exactly as described for **3** and the products were separated into phenolic and nonphenolic fractions. The nonphenolic fraction, after PLC purification, gave the amorphous **7** (120 mg): NMR δ 2.53 (s, 3 H, NMe), 3.75 (s, 3 H, OMe), 3.83 (s, 3 H, OMe), 6.08 (s, 1 H), 6.60 (s, 1 H), 6.81 (d, *J* = 9 Hz, 2 H), 7.08 (d, *J* = 9 Hz, 2 H). The oxalate of **7** crystallized from ethanol–ether: mp 135–136 °C; $[\alpha]_D$ +94° (*c* 0.80, $CHCl_3$); mass spectrum *m/e* (rel intensity) 330 (M^+, 4), 209 (100), 192 (50), 191 (40).

The phenolic fraction, after PLC purification, gave **10** (70 mg) as a colorless oil, the oxalate of which was crystalline. It was identical in all respects with (*R*)-*O*-(trideuteriomethyl)-*N*-methylcoclaurine obtained as the phenolic product of the Na/NH_3 cleavage of **5**.

Methylation of 10. Phenol **10** was methylated with diazomethane in the usual manner to give **11**, which crystallized as the oxalate, mp 136–137 °C, $[\alpha]_D$ −95° (*c* 0.10, $CHCl_3$). The NMR values and mass spectral data for **11** were identical with those of **7**, although its rotation was of the opposite sign.

Acknowledgments. We thank the National Institutes of Health for a grant (CA-11445) in support of this work, UNESCO for a supporting fellowship, and Quaid-e-Azam University, Islamabad, Pakistan, for granting a leave of absence to one of us (R.A.). We thank B. A. Krukoff (Honorary Curator of New York Botanical Garden and Consulting Botanist of Merck Sharp and Dohme Research Laboratories) for the supply of plant material, identification of the voucher specimen, and botanical consultations. We also thank Dr. C. Costello (Massachusetts Institute of Technology) for the determination of high-resolution mass spectra.

Registry No.—**1**, 62059-36-7; **2**, 6859-66-1; **3**, 13565-64-5; **4**, 62006-12-6; **5**, 62006-13-7; **6**, 3423-02-7; **7**, 62029-55-4; **7** oxalate, 62029-56-5; **8**, 62029-57-6; **9**, 524-20-9; **10**, 62006-14-8; **10** oxalate, 62006-15-9; **11** oxalate, 62006-17-1; **12**, 57256-00-5.

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