B. Neat Pyrolysis.—The adduct **10** was heated at atmospheric pressure at the designated temperature and time (Table I), cooled to room temperature, and vacuum distilled. An alternate method was to heat the adduct under a slight vacuum, during which the exothermic rearrangement evolved a gas (vacuum decrease observed), and then to raise the temperature gradually until distillation of the colorless oil commenced.

In all cases, analytical samples were obtained by preparative glc. The conditions required, spectral data of the products, and their elemental analyses, respectively, are described below for the individual cyclohepta[*b*]thiophenes.

5-Chloro-4-methoxy-8*H*-cyclohepta[*b*]thiophene (11a) (column temperature 175°, helium flow rate 80 ml/min, retention time 18.2 min) had ir (neat) 1625 (C=C), 1225, 1025 cm^{-1} (=COC); uv max (95% EtOH) 225 nm (ϵ 21,000), 278 (8200), 360 (650); nmr (neat) δ 7.02 (s, 2, thiophene), 6.00 (d, 1, H-6), 5.40 (m, 1, H-7) 3.62 (s, 3, $-OCH_3$), 3.08 (d, 2, H-8).

Anal. Calcd for $C_{10}H_9ClOS$: C, 56.46; H, 4.26; Cl, 16.67; S, 15.07. Found: C, 56.38; H, 4.10; Cl, 16.40; S, 15.00.

5-Bromo-4-methoxy-8*H*-cyclohepta[*b*]thiophene (11b) (column temperature 170°, helium flow 140 ml/min, retention time 20 min) had ir (neat) 1630 (C=C), 1225 and 1025 cm^{-1} (=COC); uv max (95% EtOH) 225 nm (ϵ 20,700), 278 (7800), 365 (645); nmr ($CDCl_3$) δ 7.00 (s, 2, thiophene), 6.02 (d, 1, H-6), 5.47 (m, 1, H-7), 3.67 (s, 3, $-OCH_3$), 3.16 (d, 1, H-8).

Anal. Calcd for $C_{10}H_9BrOS$: C, 46.70; H, 3.53; Br, 31.08; S, 12.47. Found: C, 46.48; H, 3.40; Br, 30.77; S, 12.30.

5-Chloro-4-ethoxy-8*H*-cyclohepta[*b*]thiophene (11c) (column temperature 200°, helium flow 100 ml/min, retention time 20.2 min) had ir (neat) 1620 (C=C), 1225, and 1050 cm^{-1} (=COC); uv max (95% EtOH) 228 nm (ϵ 20,900), 282 (8000), 362 (690); nmr (neat) δ 7.00 (s, 2, thiophene), 5.95 (d, 1, H-6), 5.42 (m, 1, H-7), 3.85 (q, 2, $-OCH_2CH_3$), 3.11 (d, 2, H-8), 1.24 (t, 3, $-OCH_2CH_3$).

Anal. Calcd for $C_{11}H_{11}ClOS$: C, 58.28; H, 4.89; Cl, 15.64; S, 14.14. Found: C, 58.30; H, 4.73; Cl, 15.50; S, 14.42.

5-Bromo-4-ethoxy-8*H*-cyclohepta[*o*]thiophene (11d) (column temperature 200°, helium flow 140 ml/min, retention time 22 min) had ir (neat) 1625 (C=C), 1220, and 1025 cm^{-1} (=COC); uv max (95% EtOH) 232 nm (ϵ 20,850), 280 (7500), 365 (680); nmr ($CDCl_3$) δ 7.05 (s, 2, thiophene), 6.08 (d, 1, H-6), 5.45 (m, 1, H-7), 3.92 (q, 2, $-OCH_2CH_3$), 3.15 (d, 2, H-8), 1.30 (t, 3, OCH_2CH_3).

Anal. Calcd for $C_{11}H_{11}BrOS$: C, 48.72; H, 4.08; Br, 29.46; S, 11.82. Found: C, 48.65; H, 4.21; Br, 29.20; S, 11.71.

5-Chloro-4-methyl-8*H*-cyclohepta[*b*]thiophene (11f) (column temperature 200°, helium flow 140 ml/min, retention time 18.6 min) had ir (neat) 1630 (C=C), 3060 cm^{-1} (=CH); uv max (CH_3CN) 225 nm (ϵ 20,000), 280 (7500); nmr ($CDCl_3$) δ 7.02 (s, 2, thiophene), 6.08 (d, 1, H-6), 5.59 (m, 1, H-7), 3.12 (d, 2, H-8), 2.40 (s, 3, $-CH_3$).

Anal. Calcd for $C_{10}H_9ClS$: C, 61.06; H, 4.61; Cl, 18.02; S, 16.30. Found: C, 61.28; H, 4.71; Cl, 17.90; S, 16.27.

5-Chloro-4-phenyl-8*H*-cyclohepta[*b*]thiophene (11g) (column temperature 200°, helium flow 180 ml/min, retention time 21 min) had ir (neat) 1630 (C=C), 3060 cm^{-1} (=CH); uv max (CH_3CN) 230 nm (ϵ 22,000), 270 (8600); nmr ($CDCl_3$) δ 7.18 (s, 5, C_6H_5), 6.52 (q, 2, thiophene), 6.10 (d, 1, H-6), 5.55 (m, 1, H-7), 3.18 (d, 2, H-8).

Anal. Calcd for $C_{15}H_{11}ClS$: C, 69.62; H, 4.28; Cl, 13.70; S, 12.38. Found: C, 69.69; H, 4.39; Cl, 13.87; S, 12.40.

5-Bromo-4-phenyl-8*H*-cyclohepta[*b*]thiophene (11h) (column temperature 200°, helium flow 200 ml/min, retention time 16 min) had ir (neat) 1625 (C=C), 3060 cm^{-1} (=CH); uv max (CH_3CN) 230 nm (ϵ 22,200), 275 (8500); nmr ($CDCl_3$) δ 7.28 (s, 5, C_6H_5), 6.60 (d, 2, thiophene), 6.30 (d, 1, H-6), 5.53 (m, 1, H-7), 3.15 (d, 2, H-8).

Anal. Calcd for $C_{15}H_{11}BrS$: C, 59.41; H, 3.65; Br, 26.36; S, 10.57. Found: C, 59.68; H, 3.89; Br, 26.04; S, 10.33.

Registry No.—**3a**, 36914-02-0; **3b**, 28857-19-4; **4a**, 36914-04-2; **4b**, 28857-20-7; **4c**, 36914-06-4; **4d**, 36914-07-5; **4e**, 36914-08-6; **5a**, 36914-09-7; **5b**, 36914-10-0; **5c**, 36914-11-1; **10a**, 36914-12-2; **10b**, 36914-13-3; **10c**, 28857-21-8; **10d**, 36914-15-5; **10f**, 36914-16-6; **10a**, 36914-17-7; **10h**, 36895-15-5; **11a**, 36917-68-7; **11b**, 36917-69-8; **11c**, 28857-22-9; **11d**, 36917-71-2; **11f**, 36917-72-3; **11g**, 36917-73-4; **11h**, 36917-74-5.

Notes

New Phenolic Hasubanan Alkaloids from *Stephania abyssinica*[1]

S. MORRIS KUPCHAN,* ANDRIS J. LIEPA, AND TETSURO FUJITA

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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Stephania abyssinica Walp. is a creeping plant indigenous to southern and eastern Africa which is reputed to possess a variety of medicinal uses.[2] An examination of *S. abyssinica* from Natal revealed the presence of an alkaloid[3] subsequently characterized as metaphanine (**1b**).[4] Earlier studies in this laboratory of roots and rhizomes from Ethiopia resulted in isolation and structural elucidation of the alkaloids oxoxylopine[5] ("lanuginosine"[6]) and stephavanine.[7] We report herein the isolation and structure elucidation of three new phenolic hasubanan alkaloids, stephabyssine (**1a**), stephaboline (**2**), and prostephabyssine (**3a**).

A concentrated ethanolic extract of *S. abyssinica* roots and rhizomes was partitioned between 5% hydrochloric acid and chloroform (fraction A). The acid solution was partially basified to pH 5 with ammonium hydroxide and extracted with chloroform to yield fraction B. Further basification with excess am-

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monium hydroxide and extraction with chloroform yielded fraction C.

Fraction C was absorbed on silica and the alkaloids were eluted with chloroform containing methanol. The material eluted with 1% methanol in chloroform was crystallized from aqueous ethanol to give stephabyssine (**1a**) as colorless needles: $C_{18}H_{21}NO_5$; mp 178–180°; $[\alpha]^{25}D$ −58.9° (*c* 0.87, $CHCl_3$); *m/e* 331 (M^+), 316, 231, 198; λ_{max}^{MeOH} 284 nm (ϵ 3300). The ir spectrum of **1a** showed absorption at 5.77 μ, indicative of a saturated ketone, while in the nmr spectrum signals were observed at τ 3.32 (2 H, s, aromatic H), 3.98 (s) and 4.87 (s) (2 OH), 4.98 (1 H, d, J = 6 Hz), 6.11 (3 H, OCH_3), and 7.41 (3 H, NCH_3). The presence of a phenolic hydroxyl group with an unsubstituted para position was suggested by a positive reaction of the compound with Gibbs reagent and supported by a 0.3 ppm shift of one aromatic proton in the nmr spectrum (MeOH) upon formation of the phenoxide ion.[8] This alkaloid was further characterized as the hydrochloride: mp 247–250° dec; $[\alpha]^{25}D$ − 32.5° (*c* 0.41, 60% aq EtOH).

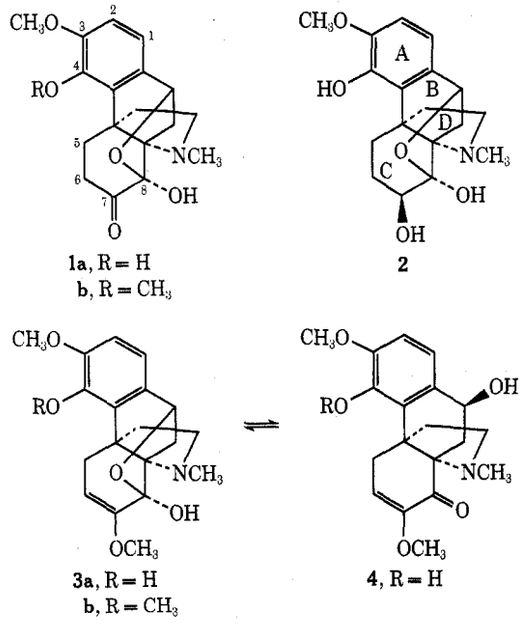
Methylation of **1a** with methyl iodide in the presence of potassium carbonate gave metaphanine (**1b**), identified by comparison of physical constants (mass spectrum, melting point, $[\alpha]D$, ir) observed for the product with reported values.[9] This conversion established the structure of stephabyssine as 4-demethylmetaphanine (**1a**).

Further elution with an increase in the proportion of methanol in the eluting solvent gave, after additional chromatography on neutral alumina, a crystalline alkaloid hydrochloride: $C_{18}H_{24}NO_5Cl$; mp 230–232° dec ($MeOH–CHCl_3$); $[\alpha]^{25}D$ +23.1° (*c* 0.44, MeOH), −45° (*c* 0.8, pyridine). Treatment with potassium carbonate liberated stephaboline (**2**): $C_{18}H_{23}NO_5$; mp 186–188° dec (aq MeOH); $[\alpha]^{25}D$ +34.7° (*c* 0.47, MeOH); λ_{max}^{MeOH} 281 nm (ϵ 2760).

The close relationship of stephaboline with **1a** was indicated by similarities in their nmr spectra as well as the positive reaction shown by each compound to ferric chloride and to Gibbs reagent. The presence of an additional hydroxyl proton signal at τ 5.24 in the nmr spectrum of **2**, when considered together with the absence of carbonyl absorption in its ir spectrum, suggested **2** was a dihydro derivative of **1a**. This proposal was readily confirmed by the high yield (78%) conversion of **1a** into **2** by reduction with sodium borohydride. The stereoselective hydride delivery observed in the course of the reduction is noteworthy but not unexpected in view of the previously demonstrated[7,10] influence exerted by steric effects during the reduction of other hasubanan ketones.

This conversion of **1a** into **2** established the structure and absolute stereochemistry of **2** as well as the relative stereochemistry at all centers with the exception of C-7. The relative inflexibility of the C ring in the molecule of **2** associated with the hemiketal superstructure permitted the stereochemistry at C-7 to be assigned on the basis of nmr measurements. The nmr spectrum of **2** (pyridine-d_5) showed an isolated diffuse multiplet centered at τ 5.6, assignable to the C-7 proton [$-CH_2CH(OH)-$], which was resolved into a pair of doublets by addition of deuterium oxide. Coupling constant values of J_{AX} = 5 Hz and J_{BX} = 11 Hz were associated with this signal. The high value of H_B–H_X coupling constant indicates involvement of the C-7 proton in axial–axial coupling and consequently favors assignment of equatorial (β) orientation to the hydroxyl group.

Chromatography of extract B upon silica succeeded by preparative layer chromatography upon silica gave an amorphous base, shown to be homogeneous by tlc in a variety of solvent systems. The alkaloid (prostephabyssine, **3a**) showed M^+ 345 ($C_{19}H_{23}NO_5$) in its mass spectrum, and ir absorption at 2.84 (OH), 5.98 (C=O), and 6.10 (broad, enolic C=C). A positive reaction with Gibbs reagent suggested the presence of a phenolic function with an unsubstituted para position. The alkaloid formed a crystalline methiodide: $C_{20}H_{24}INO_5$; $[\alpha]^{24}D$ − 105° (*c* 1.98, MeOH); λ_{max}^{KBr} 2.96 (OH), 5.94 (C=O) μ. Upon brief treatment of **3a** with aqueous hydrochloric acid, the crystalline product which was obtained in high yield was shown to be identical with **1a** by nmr, ir, melting point, and mixture melting point measurements. This facile hydrolysis of **3a** with loss of the elements of methanol to give **1a** demonstrated the presence of a labile enol ether located at C-6–C-7 and consequently supported assignment of the prostephabyssine structure **3a**. Determinations of the nmr spectra of prostephabyssine in a variety of solvents gave complex patterns indicative of the presence of the hemiketal **3a** and ketone **4** forms in equilibria similar to the solvent-dependent equilibria observed by Tomita, *et al.*,[11] for prometaphanine **3b**.[12]



1a, R = H
b, R = CH_3

2

3a, R = H
b, R = CH_3

4, R = H

Experimental Section

Melting points were determined on a Mettler FP2 melting point apparatus. Ir spectra were determined on a Perkin-Elmer 337 double beam recording spectrophotometer. Uv spectra were determined on a Beckman DK-2A recording spectrophotometer.

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(9) M. Tomita, T. Ibuka, Y. Inubushi, and K. Takeda, *ibid.*, 3605 (1964).
(10) S. M. Kupchan and M. I. Suffness, *ibid.*, 4978 (1970).
(11) M. Tomita, T. Ibuka, and Y. Inubushi, *Tetrahedron Lett.*, 3617 (1964).
(12) We have also isolated prostephabyssine (**3a**) from *Stephania hernandifolia*.

Nmr spectra were determined on a Varian Associates HA-100 spectrometer on solutions in $CDCl_3$ with TMS as internal standard. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. Mass spectra were measured on a Hitachi-Perkin-Elmer RMU-6E spectrometer.

Extraction and Preliminary Fractionation.—The dried ground roots and rhizomes (5.5 kg) of *S. abyssinica* were continuously extracted with hot 95% ethanol during 24 hr, and the extract was concentrated *in vacuo* to 1 l. The concentrate was dissolved in chloroform and extracted twice with 5% HCl (total of 4 l.). The organic phase was separated and evaporated to yield fraction A (74 g). The acid solution was decanted from an insoluble tar (101 g), adjusted to pH 5.0 with NH_4OH, and extracted twice with chloroform (1 l.). The resultant chloroform solution of weak bases yielded fraction B (73 g) upon evaporation. An excess of NH_4OH added to the remaining aqueous phase precipitated the strong bases which were extracted twice with chloroform (1 l.) to give fraction C (25 g).

Stephabyssine (1a).—A portion of extract C (15 g) was chromatographed over 400 g of silica gel (0.05–0.2 mm, Merck) in chloroform. Elution was begun with 1% methanol–chloroform, and subsequent to a dark-colored forerun, eluate (2 l.) was collected and evaporated. The residue was twice crystallized from aqueous ethanol to give stephabyssine (**1a**) (271 mg): mp 178–180°; $[\alpha]_D$ −58.9° (*c* 0.87, $CHCl_3$); λ_{max}^{KBr} 2.82, 5.77 μ; λ_{max}^{MeOH} 284 nm (ε 3300); *m/e* (%) 331 (M^+, 26), 316 (2.5), 231 (100), 198 (19); nmr τ 3.32 (s, 2 H, aromatic), 3.98 (s) and 4.87 (s) (2 OH), 4.98 (d, 1 H, *J* = 6 Hz), 6.11 (s, 3 H, OCH_3), 7.41 (s, 3 H, NCH_3).

Anal. Calcd for $C_{18}H_{21}NO_5$: C, 65.24; H, 6.39; N, 4.23. Found: C, 65.15; H, 6.29; N, 4.43.

Stephabyssine Hydrochloride.—Stephabyssine (40 mg) was stirred with 10% hydrochloric acid (1 ml) for 4 hr, the mixture evaporated to dryness *in vacuo*, and the residue crystallized twice from chloroform–carbon tetrachloride to give the hydrochloride (41 mg) as colorless plates: mp 247–250° dec; $[\alpha]^{25}D$ −32.5° (*c* 0.41, 60% aq EtOH); λ_{max}^{KBr} 3.05, 3.99, 5.79, 7.78, 8.73 μ.

Anal. Calcd for $C_{18}H_{21}NO_5 \cdot HCl$: C, 58.78; H, 6.03; N, 3.81. Found: C, 58.77; H, 6.03; N, 3.81.

Methylation of Stephabyssine (1a) to Metaphanine (1b).—Anhydrous potassium carbonate (200 mg) was added to a suspension of stephabyssine (50 mg) in methanol (1.5 ml) containing methyl iodide (0.3 ml). The mixture was allowed to stand 18 hr and then filtered and the solid washed thoroughly on the filter with water followed by a little methanol. Recrystallization from chloroform–ether gave colorless prisms (24 mg), mp 230–232° dec, charactarized by melting point, optical rotation, and ir, nmr, and mass spectrum as metaphanine by comparison with reported values.[9]

Stephaboline (2) Hydrochloride.—Elution was continued with 2, 3, 4, 5, and 6% methanol–chloroform (2 l. each); the eluates containing 5 and 6% methanol were combined and after evaporation the residual material was rechromatographed on 80 g of neutral alumina (activity I, Merck) overlaid with 10 g of basic alumina (activity I, Merck). After preliminary elution with chloroform (300 ml), 300-ml portions of chloroform containing 2, 4, and 5% ethyl acetate were passed through the column. The ethyl acetate containing eluates were combined and the solvents evaporated; the residue was taken up in 50% benzene–chloroform (20 ml) and allowed to stand overnight. Recrystallization of the precipitate from methanol–chloroform gave stephaboline hydrochloride (48 mg): mp 230–232° dec; $[\alpha]^{25}D$ +23.1 (*c* 0.44, MeOH), −45° (*c* 0.8, pyridine); λ_{max}^{KBr} 2.92, 2.99, 3.10, 3.71, 7.82 μ; λ_{max}^{MeOH} 283 nm (ε 2940).

Anal. Calcd for $C_{18}H_{23}NO_5 \cdot HCl$: C, 58.46; H, 6.54; N, 3.79; Cl, 9.59. Found: C, 58.58; H, 6.47; N, 3.64; Cl, 9.39.

Stephaboline (2).—Potassium carbonate (100 mg) was added to a solution of stephaboline hydrochloride (20 mg) in 50% aqueous methanol (2 ml), the mixture stirred 10 min, and 10 ml of water added. After 16 hr the precipitate was collected and crystallized from aqueous methanol to give stephaboline (11 mg): mp 186–188° dec; $[\alpha]^{25}D$ +34.7° (*c* 0.47, MeOH); λ_{max}^{EtOH} 281 nm (ε 2760); λ_{max}^{KBr} 2.79, 3.07, 6.64, 9.15, 9.57 μ; *m/e* (%) 333 (M^+, 17), 257 (12), 230 (100), 215 (9), 198 (33), 196 (16); nmr τ (pyridine-d_5) 3.34 (s, 2 H, aromatic), 4.06 (s), 4.81 (s), and 5.24 (s), (3 × 1 H, OH), 5.04 (d, 1 H, *J* = 6 Hz), 5.62 (dd, 1 H, *J* = 5 Hz, *J* = 11 Hz), 6.32 (s, 3 H, OCH_3), 7.23 (s, 3 H, NCH_3).

Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.84; H, 7.02; N, 3.98.

Stephaboline Methiodide.—A suspension of stephaboline (60 mg) in chloroform (8 ml) containing methyl iodide (2 ml) was stirred for 24 hr. The colorless prisms were filtered and recrystallized from methanol–ethyl acetate (42 mg): mp 230–232° dec; $[\alpha]^{25}D$ +19.6° (*c* 0.51, MeOH); λ_{max}^{KBr} 2.98, 6.20, 7.81, 9.42 μ.

Anal. Calcd for $C_{18}H_{23}NO_5 \cdot CH_3I$: C, 48.01; H, 5.51; N, 2.95. Found: C, 48.02; H, 5.59; N, 3.04.

Borohydride Reduction of Stephabyssine.—Sodium borohydride was added in eight portions (50 mg each) during 2 hr to a stirred suspension of stephabyssine (450 mg) in 50% aqueous methanol (15 ml). After a further 0.5 hr, 20% aqueous methanol (10 ml) was added and the mixture stirred 2 hr. The crystalline precipitate was collected, washed with 10% aqueous methanol, and recrystallized from methanol to give colorless needles (330 mg) of **2**, characterized by melting point, mixture melting point, and nmr comparison with stephaboline.

Prostephabyssine (3a).—Extract B (48 g) was stirred with 80% ethyl acetate–chloroform (500 ml) until no further material dissolved. After removal of the insoluble components the solvents were evaporated, and the residue was chromatographed over 1.5 kg of silica gel (0.2–0.05 mm, Merck). After elution with chloroform (4 l.), followed by chloroform containing 1, 2, and 4% methanol (4 l. of each), chromatography was continued with chloroform containing 6% methanol (8 l.). After evaporation of the solvents from the latter eluate, the residue was stirred with ethyl acetate (100 ml), the mixture filtered, and the filtrate evaporated. The residue in chloroform was applied to preparative layer silica gel plates (20 × 20 cm, 0.2 cm absorbent layer, Merck F_{254}) which were subsequently eluted with 4% methanol–chloroform. The principal low R_f band was collected and then extracted with 20% methanol–chloroform, and the filtered extract was evaporated to dryness to give prostephabyssine (**3a**) (200 mg) as a pale yellow glass, $\lambda_{max}^{CHCl_3}$ 2.84, 5.98, 6.10 μ.

Prostephabyssine Methiodide.—A solution of prostephabyssine, (**3a**, 80 mg) in benzene (1 ml) containing methyl iodide (0.5 ml) was refluxed 20 min and allowed to stand overnight at room temperature. Recrystallization of the precipitate from methanol–benzene gave colorless prisms (47 mg): mp 196–198° dec; $[\alpha]^{25}D$ −105° (*c* 1.98, MeOH); λ_{max}^{MeOH} 282 nm (ε 3810); λ_{max} 2.95, 5.90 μ.

Anal. Calcd for $C_{19}H_{23}NO_5 \cdot CH_3I$: C, 49.29; H, 5.34; N, 2.87. Found: C, 49.04; H, 5.22; N, 2.84.

Acid Hydrolysis of Prostephabyssine (3a) to Stephabyssine (1a).—A solution prostephabyssine (**3a**, 41 mg) in 50% acetone–methanol (2 ml) containing 5% hydrochloric acid (0.6 ml) was warmed on the steam bath for 5 min. After removal of the volatile materials *in vacuo* the residue was basified with ammonium hydroxide and extracted with chloroform (20 ml). After evaporation of the chloroform, the residue was twice crystallized from methanol–acetone to give colorless needles of **1a** (24 mg), characterized as stephabyssine by melting point, mixture melting point, and ir and nmr comparison with an authentic sample.

Registry No.—**1a**, 36871-84-8; **1a** HCl, 36871-85-9; **2**, 36871-86-0; **2** HCl, 36921-52-5; **2** MeI, 36871-87-1; **3a**, 36871-88-2; **3a** MeI, 36921-53-6.

The West Synthesis of Hexabromocyclopentadiene

GARY A. UNGEFUG

Hydrocarbons and Monomers Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640

CARLETON W. ROBERTS*[1]

Textile Department, Clemson University, Clemson, South Carolina 29631

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Until the publication of the West procedure for the synthesis of hexabromocyclopentadiene (II) from

(1) To whom inquiries should be directed.