sulted from thermal equilibration, but we now find that our attempts to trap the isomer formed first lead us to the conclusion opposite to that in the earlier report.[3] In our hands the reaction follows path A and **2** is at least the predominant product of this reaction.

A sample of the methylbicyclopentene **1** was divided in two parts and one part was dissolved in tetrahydrofuran and the other in chloroform-*d*, each solvent containing an excess of *N*-phenylmaleimide. The samples were placed in a bath at 43°, and the progress of the reaction was monitored by periodic observation of the nmr spectrum of the chloroform-*d* solution. The signals for the *N*-phenylmaleimide adduct of 2-methylcyclopentadiene were observed to grow with time, the methyl doublet at τ 8.18 and the vinyl multiplet at τ 4.24 providing a particularly useful basis for identification.[4] After 24 hr, when the reaction appeared to be complete, the product was predominantly the adduct of the 2-methyl isomer, and contained no more than 5% of the adduct of the 1-methyl isomer as judged by the strength of signals in the regions characteristic of this isomer.[4] The tetrahydrofuran solution was evaporated to dryness and the nmr spectrum of the residue showed that it was essentially the same product as that formed in the chloroform-*d* solution. Recrystallization of the residue provided a sample, mp 122–125°, which on admixture with an authentic sample of the adduct of 2-methylcyclopentadiene had mp 124–128°[6] and which was spectroscopically indistinguishable from the 2-methylcyclopentadiene adduct.

It is obviously difficult to reconcile our results with those reported previously[3] but, especially in the light of current interest in the limiting conditions for the Woodward–Hoffmann rules, it is important to find the explanation for the differences. In reactions of this type, particularly if the activation energies of the concerted and nonconcerted processes are of similar magnitude, the history of every reactant may be crucial. In the present study we have used all-glass apparatus throughout, and prior washing of the apparatus with base did not appear to influence the result. None of the reactants was in the presence of any metal, and the bicyclopentene **1** was not purified by vapor phase chromatography as formerly;[2] instead **1**, prepared photochemically from methylcyclopentadienes, was freed from unchanged dienes by treating the mixture with excess *N*-phenylmaleimide in anisole and distilling the unreacted material at low pressure. This process was repeated until the nmr spectrum of the distillate showed no trace of methylcyclopentadienes. The tetrahydrofuran used was carefully purified and redistilled from lithium aluminum hydride immediately before use. In some runs the thermal rearrangement was carried out in the presence of a base, pyridine, or 1,8-bis(dimethylamino)naphthalene (Aldrich's "Proton Sponge"), but no significant difference in the distribution of isomers was observed in the product.

It should be noted that our result does not provide a decisive answer to the question of whether the rearrangement of the bicyclopentene is concerted or not. Although evidence has been presented[2,3] that the starting methylbicyclopentene is the 2-methyl isomer **1**, a small amount of the 1-methyl isomer could nevertheless be present in equilibrium with **1**, and the possibility that the reaction proceeds through the 1-methyl isomer cannot be completely ruled out. Furthermore, although the formation of **2** can most readily be explained by a nonconcerted opening of **1**, a concerted [$_{\sigma}2_{s} + {}_{\sigma}2_{a}$] process, corresponding to that invoked previously[3] but with the migrating methylene group moving exclusively in the opposite direction (*i.e.*, to C-3 of **1**) to that required to form **3**, could also lead to **2**. It appears that a bicyclopentene with suitable double labeling will be required to resolve this ambiguity.

Acknowledgment. This work was supported by an operating grant from the National Research Council of Canada.

(6) Fractional crystallization of the mixture of adducts obtained from the equilibrium mixture of **2** and **3** affords first the adduct of **3**, less soluble in common solvents, and this can be recrystallized to a high degree of purity (mp 179–180°). Later fractions yield material, mp ~114°, which is a constant melting mixture of the adducts of **2** (major component) and **3**. Recrystallization of this does not raise the melting point, but the diene **2**, purified by vpc, forms an adduct, mp 128–129.5°.[4]

(7) Holder of National Research Council of Canada Graduate Scholarship, 1968–1971.

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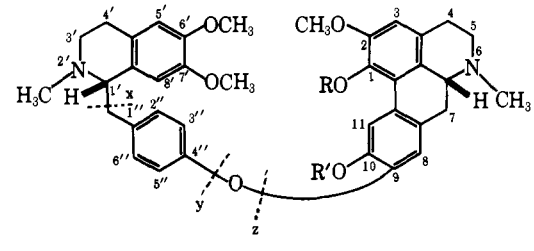
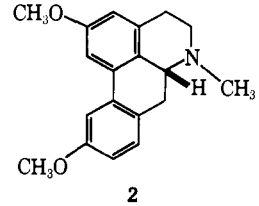
Pakistanine and Pakistanamine, Two Novel Dimeric Isoquinoline Alkaloids[1]

Sir:

We wish to report the isolation and structural elucidation of the phenolic aporphine benzylisoquinoline alkaloid pakistanine (**1a**) found in *Berberis baluchistanica* Ahrendt (Berberidaceae): $C_{37}H_{40}O_6N_2$; mp 156°; $[\alpha]^{28}D$ +106° (MeOH).[2]



1a, R = R′ = H
1b, R = R′ = CH_3
1c, R = CH_3; R′ = H



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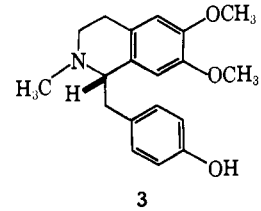

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O-Methylation of pakistanine **1a** with diazomethane yielded *O,O*-dimethylpakistanine (**1b**): $C_{39}H_{44}O_6N_2$;

(1) This research was supported by Grant No. 1RO1 CA11450 from the National Institutes of Health to M. S., and by a free grant from the Hoffmann-La Roche Foundation. The authors are grateful to Professor M. Tomita for a sample of authentic 2,10-dimethoxyaporphine.

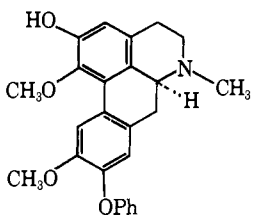
(2) The plant was collected in the northern regions of West Pakistan, and was identified by Dr. A. R. Beg, Plant Taxonomist, Forest Research Institute, Peshawar, Pakistan. Elemental formulas were determined by high-resolution mass spectral analyses.

mp 137°. Comparison of the mass spectrum of **1a**, *m/e* 608 (M^+), 402 (M − x), 312 (M − y), 296 (M − z), and 206 (x, base), with that of **1b**, *m/e* 636 (M^+), 430 (M − x), 340 (M − y), 324 (M − z), and 206 (x, base), established that **1a** possessed a diphenolic aporphine moiety bonded through a diphenyl ether linkage to an armepavine-like residue.

The nmr spectrum of pakistanine **1a** in $CDCl_3$ exhibits a high-field methoxyl singlet absorption at δ 3.61 (3 H, C-7′OC*H*$_3$), two methoxyl singlets at 3.83 and 3.88 (6 H), two *N*-methyl singlets at 2.51 and 2.56 (6 H), a singlet at 6.06 (1 H, C-8′*H*), three aromatic proton singlets at 6.54, 6.56, and 6.71 (3 H), an A_2B_2 quartet (4 H) at 7.00 (J = 8.5 and 10 Hz) (C-2″, -3″, -5″, and -6″*H*), and a one-proton singlet at 8.11 (C-11*H*). The nmr spectrum of *O,O*-dimethylpakistanine (**1b**) shows two additional methoxy resonances, one at δ 3.72 and the other at 3.90, the former being characteristic of a C-1 methoxyl.[3] The remainder of the spectrum of **1b** is very similar to that of **1a**. The phloroglucinol test for an *o*-diphenol function[4] was negative for pakistanine **1a**, so that a methoxyl group could be assigned to the C-2 position.

Sodium in liquid ammonia cleavage of *O,O*-dimethylpakistanine (**1b**) yielded (−)-2,10-dimethoxyaporphine (**2**)[1] and L-(+)-armepavine (**3**).

The uv spectrum of pakistanine **1a** (λ_{max}^{EtOH} 218, 270 sh, 277, and 307 nm (log ϵ 4.61, 4.13, 4.21, and 4.07)) resembles that of 9-phenylboldine (**4**),[5] C_{25}-



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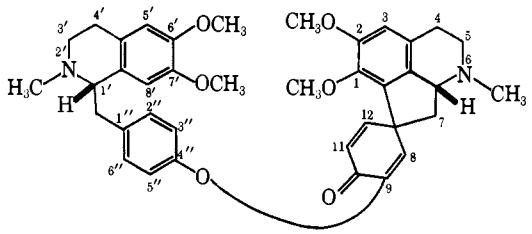

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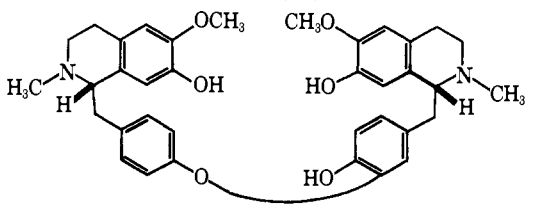
$H_{25}O_4N$, mp 155–157° (λ_{max}^{EtOH} 218, 270 sh, 276, and 303 nm (log ϵ 4.30, 4.23, 4.25, and 3.82)).

From the same plant source we have also obtained the first known proaporphine benzylisoquinoline alkaloid, pakistanamine (**5**): $C_{38}H_{42}O_6N_2$; mp 158–162° dec (picrate); mp 215° (hydrochloride); amorphous free base; $[\alpha]^{25}D$ +20° (MeOH).

The ir spectrum, ν^{CHCl_3} 1640 (C=C) and 1670 cm^{-1} (conjugated C=O), and the uv spectrum, λ_{max}^{EtOH} 225 sh, 280, and 310 sh nm (log ϵ 4.63, 4.12, and 3.61), of pakistanamine (**5**) were suggestive of the presence of a dienone moiety.[6] The nmr spectrum of pakistanamine (**5**) in $CDCl_3$ showed four methoxyl singlets at δ 3.57, 3.64, 3.80, and 3.82 (12 H), two *N*-methyl singlets at 2.32 and 2.35 (6 H), a singlet at 6.07 (1 H, C-8′*H*), a doublet at 6.16 (1 H, $J_{8,12}$ = 2.5 Hz, C-8*H*), a doublet at 6.32 (1 H, $J_{11,12}$ = 10 Hz, C-11*H*), a doublet of doublets at 7.06 (1 H, J = 2.5 and 10 Hz, C-12*H*), singlets at 6.55 and 6.62 (2 H, C-3 and C-5′*H*), and finally a singlet at 7.02 (4 H, C-2″, -3″, -5″ and -6″*H*).

Dienone–phenol rearrangement of pakistanamine **5** using dilute HCl gave rise to the phenolic aporphine benzylisoquinoline dimer **1c**: $C_{38}H_{42}O_6N_2$; mp 117°; $[\alpha]^{25}D$ −103° (MeOH). The uv spectrum of **1c**, λ_{max}^{EtOH} 225 sh, 267 sh, 277, and 304 nm (log ϵ 4.75, 4.28, 4.37, and 4.16), closely resembles that of pakistanine **1a**, and indeed *O*-methylation of **1c** with diazomethane furnished the product **1b**, identical in terms of melting point, mixture melting point, uv, ir, nmr, and mass spectra, tlc R_f values, and ORD curve with a sample of *O,O*-dimethylpakistanine derived by O-methylation of pakistanine **1a**.

The fact that pakistanine and pakistanamine are found in the same plant lends substantial support to the biogenetic scheme involving the sequence: bisbenzylisoquinoline → proaporphine benzylisoquinoline dimer → aporphine benzylisoquinoline dimer.[7] Noteworthy also is the observation that the required bisbenzylisoquinoline precursor in the present instance corresponds to the alkaloid (+)-berbamunine (**6**) found



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in *B. amurensis* Rupr. var. *japonica*,[8] a close relative of *B. baluchistanica*.

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(4) H. A. Schroder, *J. Chromatogr.*, **30**, 537 (1967).

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Reduction of Acetylene and Nitrogen by a Cobalt–Porphyrin System

Sir:

Since the successful isolation and purification of nitrogenase, the enzyme system that fixes molecular nitrogen to ammonia in living organisms, many studies have been made to find a model for nitrogenase action.[1-3] We present in this paper the description of a

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