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11-Methoxyakuammicine from *Alstonia muelleriana*

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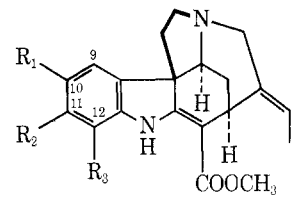
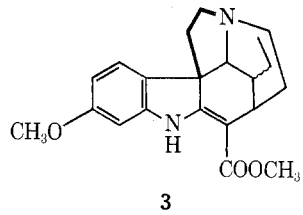
In our recent investigation of the alkaloids of *Alstonia muelleriana*[1] the isolation of a methoxyakuammicine alkaloid was reported. From spectral data, but without a direct comparison with authentic material, this alkaloid was judged to be identical with vinervinine (**1**), which had been isolated from *Vinca erecta* and assigned structure **1**, 11-methoxyakuammicine, by Yunusov and his coworkers.[2,3]





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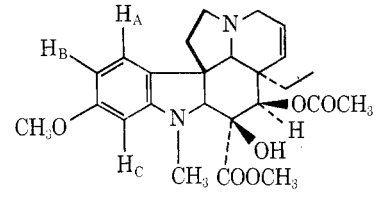
1, $R_1 = R_3 = H$; $R_2 = OCH_3$
2, $R_1 = R_2 = H$; $R_3 = OCH_3$
4, $R_1 = OH$; $R_2 = R_3 = H$;
9-H = H_A; $R_2 = H_B$; $R_3 = H_C$



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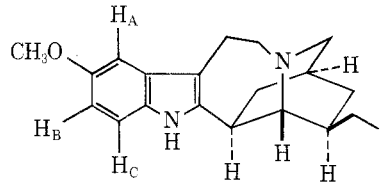

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Very recently,[4] the proposed structure 1 for vinervinine has been revised by Yunusov and coworkers to 12-methoxyakuammicine (**2**). We wish now to distinguish our alkaloid from vinervinine, and to support our original assignment of structure 1 to the compound from *A. muelleriana*.

The uv spectrum of our compound shows λ_{max} (MeOH) 232, 252 (sh), 298, 325 nm (ϵ 11,500, 9300, 7000, 6700), λ_{min} 272, 312 nm (ϵ 5600, 6400), which differs slightly from that which we reported previously.[1] These data are in better accord with those for 11-methoxy-14,19-dihydrocondylocarpine (**3**)[5] [λ_{max} (EtOH) 255, 286, 327 nm (ϵ 14,800, 10,900, 11,200), λ_{min} 275, 310 nm (ϵ 9500, 10,200)] than those for vinervinine [λ_{max} 237, 292, 334 nm (ϵ 13,000, 6600, 26,500)].[3] However, the definitive evidence for position assignment among phenolic functions of these alkaloids is from the NMR spectra of the aromatic region, as we have shown for sewarine (**4**, 10-hydroxyakuammicine),[6] the structure of which has also been confirmed crystallographically.[7]

Table I shows a comparison between the NMR spectra in the aromatic region for several indole alkaloids. It is clear that the spectrum of our alkaloid is very similar to those of vindoline (**5**) and 11-methoxy-14,19-dihydrocondylocarpine (**3**), but different from those for sewarine (**4**) and ibogaine (**6**). In particular, the spectrum in acetone-d_6 is especially revealing, and unequivocally indicates the identity of

Table I
NMR Spectra (Aromatic Region) of Hydroxy- and Methoxyindole Alkaloids

Alkaloid	H_A, τ	J_{AB}, Hz	H_B	J_{BC}	H_C	Solvent	Ref
Vindoline (**5**)	3.09	8	3.70	2	3.92	$CDCl_3$	6
Ibogaine (**6**)	3.05	2	3.25	9	2.92	$CDCl_3$	6
Sewarine (**4**) HCl	3.02	2	3.30	7	3.17	CD_3OD	6
11-Methoxy-14,19-dihydrocondylocarpine (**3**)	3.02	9	3.5–3.8, 2 H multiplet			Probably $CDCl_3$	5
11-Methoxyakuammicine (**1**)[8]	3.0	8	~3.3, 2 H multiplet			$CDCl_3$	Present work and ref 1
	2.65	8	3.5	2	3.3	CD_3COCD_3	

substitution pattern between our alkaloid and vindoline.[8] The spectra of 2,16-dihydrovinervinine and *N*-acetyldihydrovinervinine published in pictorial form by Yunusov et al.[4] are very different from any of these.

The evidence for the akuammicine skeleton in the alkaloid from *Alstonia muelleriana* has been summarized previously.[1] From these data and the evidence discussed above we wish to retain the structure 11-methoxyakuammicine (for which a new trivial name seems unnecessary) for this alkaloid.

Acknowledgment. We thank Professor James P. Kutney for discussions.

Registry No.—**1**, 54484-54-7.

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(8) In $CDCl_3$, H_A appeared as a doublet (J = 8 Hz) at τ 3.0, while H_B and H_C gave superimposed signals at ca. τ 3.3. However, when the spectrum was repeated in acetone-d_6 the 1,2,4 pattern reminiscent of vindoline was quite clear (H_A, doublet, J = 8 Hz; H_B, doublet of doublets, J_{AB} = 8 Hz, J_{BC} = 2 Hz; H_C, doublet, J = 2 Hz).

Reactions of Dichlorocarbene with Methylenecyclohexan-4-one Ethylene Thioacetals

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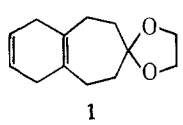
"Synergistic" carbenic cyclopropanation is dramatically illustrated by the Simmons–Smith reaction, in which a zinc carbenoid is intercepted by an hydroxyl, alkoxyl, or oxo substrate functionality, and the methylene fragment is subsequently transferred to a nearby π bond. Augmented addition rates and stereochemical control are observed in such reactions.[2,3] Substrate-assisted cyclopropanation is rarely observed with other carbenic species, however, and our attention was drawn to the suggestion that CCl_2 could be delivered to the central π bond of **1** by prior coordination to an oxygen atom, resulting in a threefold reactivity advantage of the central over the peripheral π bond.[4]



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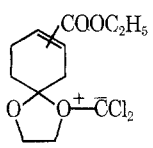

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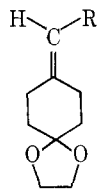


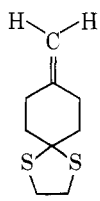
3a, R = H
b, R = $COOC_2H_5$

Unfortunately, no synergism could be detected in CCl_2 additions to various oxygen-functionalized cyclohexene derivatives,[5-7] including those in which the olefinic carbons were activated toward possible Michael addition of an anionic fragment representing a "trapped" CCl_2; cf. **2**.[7]

Addition–displacement cyclopropanations passing through **2**, or analogs, would require front-side displacement of the CCl_2 moiety from the oxygen carrier to complete the cyclopropanation.[8] The forbidden character of such displacements[9] could explain the observed lack of synergism. Moving the acceptor π bond from an endocyclic to an exocyclic position would obviate this problem, but CCl_2 additions to methylenecyclohexan-4-one ethylene acetals, **3**, were also found to occur without synergistic involvement of the acetal function.[10] Either oxygen atoms competed poorly with π bonds as sites for attack by the highly selective CCl_2,[11] or O-ylides which did form followed alternative, lower energy pathways in preference to addition–displacement.

On the other hand, S atoms do compete intramolecularly with π bonds for CCl_2. Whereas reaction of CCl_2 with allyl ethyl ether gave no evidence for O-ylide derived products,[12] S-ylide derived products were formed in reactions of CCl_2 with allylic sulfides.[13,14] Indeed, S-ylides formed by carbene capture have achieved substantial importance in sigmatropic rearrangement[15] and β-elimination reactions.[16]

The obvious superiority of sulfur over oxygen as a site for carbene attack prompted us to prepare methylenecyclohexan-4-one ethylene thioacetals **4** and **5**, and to examine their reactions with CCl_2, in search of S-ylide mediated cyclopropanations.



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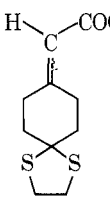

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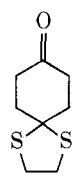

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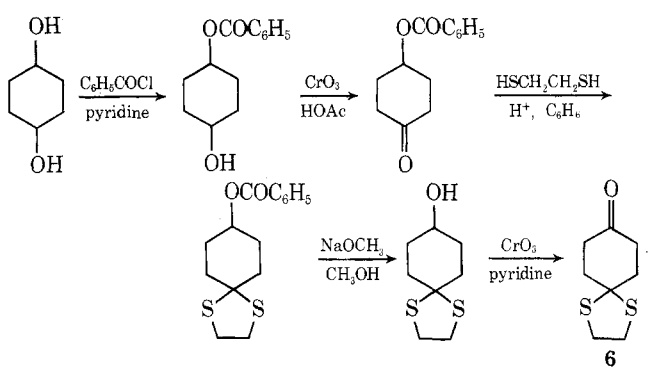
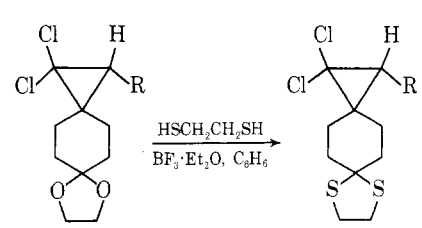
Olefinic thioacetals **4** and **5** were prepared by appropriate Wittig reactions on 1,4-cyclohexanedione monoethylene thioacetal (**6**), which was itself obtained from 1,4-cyclohexanediol by the procedure of Scheme I.

Scheme I



The CCl_2 adducts of **4** and **5** (**7** and **8**, respectively) were most readily prepared by acetal–thioacetal exchange reactions on oxygen analogs **7**-Ox and **8**-Ox, which were available in quantity from a previous study; cf. eq 1.[17]



(1)

7-Ox, R = H
8-Ox, R = $COOC_2H_5$

7, R = H
8, R = $COOC_2H_5$

Mercurial-based CCl_2 precursors[12] did not convert **4** to **7**. However, **4** with sodium trichloroacetate in refluxing monoglyme[18] afforded **7** and a yet unidentified isomer in low yield. Similar attempts to add CCl_2 to **5** were fruitless. Cyclopropane **8** could not be obtained; rather, substrate **5** was *destroyed*, leaving behind a black, high-boiling tar. Control experiments showed that authentic **8** was stable to the reaction conditions, and could be readily detected by GC in the control product mixtures.