Notes

N-Methylbicycloatalaphylline, a New Alkaloid from *Atalantia monophylla* Correâ

D. Basu and S. C. Basa*

University College of Science, Calcutta-9, India

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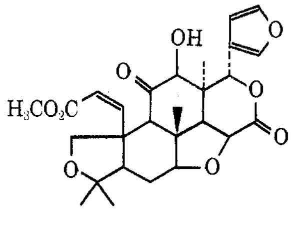
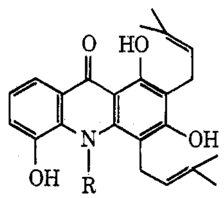
In the course of detailed analysis of the chemical constituents of *Atalantia monophylla* Correâ, a new acridone base, $C_{24}H_{27}NO_4$ (M^+ 393), has been isolated. The structure of this alkaloid has been established and is reported in the present communication.

Previous work on the roots of this botanical species collected from different parts of India by various groups of workers[1-3] did not furnish the same results. Sabata and coworkers[1] isolated the limonoid, atalantin (I), from *Atalantia* collected from Orissa and did not report the occurrence of any alkaloid, whereas Govindachari, *et al.*[2], could isolate two new acridone alkaloids, atalaphylline (IIa) and *N*-methylatalaphylline (IIb), but not atalantin (I). Xanthyletin (III) has also been reported[3] to occur in this species.

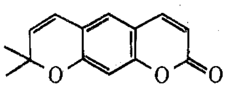
We collected the roots of the plant from Orissa, and from the petroleum ether (bp 60–80°) extract we could isolate all the aforesaid constituents besides a new alkaloid, *N*-methylbicycloatalaphylline (IV).



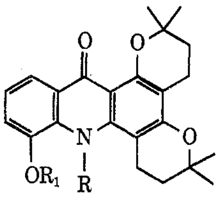
I



IIa, R = H
b, R = CH_3



III



IV, R = CH_3; R_1 = H
V, R = R_1 = CH_3
VI, R = H; R_1 = CH_3

The alkaloid *N*-methylbicycloatalaphylline, $C_{24}H_{27}NO_4$ (M^+ 393), mp 185°, appeared in the benzene eluates upon chromatographic resolution of petroleum ether extract of the roots over silica gel as well as alumina. That the base is not an artifact of its uncyclized isomer IIb was proved by the presence of tlc spots corresponding to both these bases among the seven constituents in the crude plant extract. Moreover, the isolation of this base also substantiates the earlier report by Govindachari, *et al.*,[2] of the presence of polar constituents other than atalaphylline and *N*-methylatalaphylline in the crude extract.

The alkaloid exhibited ultraviolet and infrared spectra (see Experimental Section) typical of 9-acridones and gave a positive ferric reaction, thereby indicating the presence of a phenolic hydroxyl group. This contention was further substantiated by the infrared absorption at 3475 cm^{-1}. In the nmr spectrum sharp singlets at δ 1.50 and 1.54 (6 H each) and broad multiplets at δ 1.85 and 2.80 (4 H each), respectively, were characteristic of the 2,2-dimethylchroman system. The signal of the methylimino group was clearly discernible at δ 3.94 (3 H, s) while the aromatic protons of the C_6 and C_7 locus merged with the phenolic hydroxyl at C_5 (which disappeared on D_2O exchange) as a complex multiplet at δ 7.34. The C_8 aromatic proton, deshielded by the neighboring peri carbonyl group, appeared at δ 7.8.

The mass spectrum of the alkaloid exhibited strong peaks at *m/e* 393 (M^+, 100%), 378 (M − 15), 350 (M − 43), 338 (M − 55), 322 (378 − 56), 294, 282 (338 − 56), and 268, which is in agreement with the structure IV.

On treatment with diazomethane IV formed a monomethyl ether V, $C_{25}H_{29}NO_4$ (M^+ 407), which gave superimposable ir spectra with the *N*-methyl derivative of *O*-methylbicycloatalaphylline[4] (VI), thereby confirming the structure of the new base as *N*-methylbicycloatalaphylline (IV).

Experimental Section

Melting points are uncorrected. Uv spectra were determined in a Beckman Model DU-2 and ir spectra in Perkin-Elmer 337 instruments. Nmr spectra were determined at 100 MHz in $CDCl_3$, a few drops of DMSO-d_6 being added where necessary. Tlc was done on silica gel G plates with benzene–ethyl acetate (9:1) as developer and iodine vapor as indicator.

Isolation.—The powdered root bark (5 kg) of *Atalantia monophylla* collected from the Chandka forest, Orissa, was extracted with petroleum ether (bp 60–80°). The concentrated petroleum extract on tlc examination showed seven distinct spots. The most polar constituent (R_f 0.61) showed an identical R_f value with that of pure *N*-methylbicycloatalaphylline. The crude extract was left in the refrigerator for 1 week, during which a dirty yellow solid separated out. It was filtered and repeatedly crystallized from methanol in needles, mp 185°, and was characterized as atalantin.

The concentrated mother liquor was diluted with benzene and chromatographed over silica gel (500 g). The column was eluted with solvents of increasing polarity. Fractions of about 50 ml each were collected and monitored by tlc and those giving identical spots were combined together. Xanthyletin and β-sitosterol migrated out of the column from 2 and 5% ethyl acetate in petroleum eluates, respectively. Early benzene fractions 24–30 yielded *N*-methylbicycloatalaphylline (50 mg), R_f 0.61, followed by *N*-methylatalaphylline (15 mg), R_f 0.56, from frac-

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(1) M. R. Thakar and B. K. Sabata, *Indian J. Chem.*, **7**, 870 (1969).

(2) T. R. Govindachari, N. Viswanathan, B. R. Pai, V. N. Ramachandran, and P. S. Subramanium, *Tetrahedron*, **26**, 2905 (1970).

(3) S. K. Talapatra, S. Bhattacharyya, and B. Talapatra, *J. Indian. Chem. Soc.*, **47**, 600 (1970).

(4) The authors thank Dr. N. Viswanathan for this sample.

tions 34–38 and atalaphylline (20 mg), R_f 0.42, from fractions 42–47. The latter fractions furnished a tarry mass which still showed the presence of a number of less polar components.

***N*-Methylbicycloatalaphylline.**—The alkaloid crystallized from benzene as yellow needles: mp 185°; λ_{max}^{EtOH} 228 nm (log ϵ 4.20), 274 (4.49), 340 (4.07), 420 (3.66); $\lambda_{max}^{EtOH + alkali}$ 245 nm (log ϵ 4.24), 308 (4.52), 375 (4.14); ν_{max} 3475, 1630, 1560, 1530, 1450 cm^{-1}.

Anal. Calcd for $C_{24}H_{27}NO_4$: C, 73.26; H, 6.92; N, 3.56. Found: C, 73.25; H, 6.46; N, 3.69.

Methylation of *N*-Methylbicycloatalaphylline.—A solution of IV (0.05 g) in MeOH (5 ml) was treated with excess CH_2N_2 and the product was chromatographed over silica gel, and a semisolid mass (V), homogeneous by tlc in several solvent systems, migrated out. It exhibited ν_{max}^{Nujol} 1640, 1600, 1575 cm^{-1} and a molecular ion peak (M^+) at *m/e* 407.

Methylation of *O*-Methylbicycloatalaphylline.—A solution of VI (0.02 g) in acetone (15 ml) was refluxed with MeI (2 ml) and anhydrous K_2CO_3 (0.1 g) over a steam bah for 96 hr. Usual work-up led to a gummy mass containing traces of starting material. Separation by preparative tlc over silica gel gave a semisolid mass which gave a superimposable ir spectrum with that of V.

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Valence Isomerization of 2,4,6-Trimethyl-2*H*-pyran[1]

ELLIOT N. MARVELL* AND THOMAS GOSINK

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

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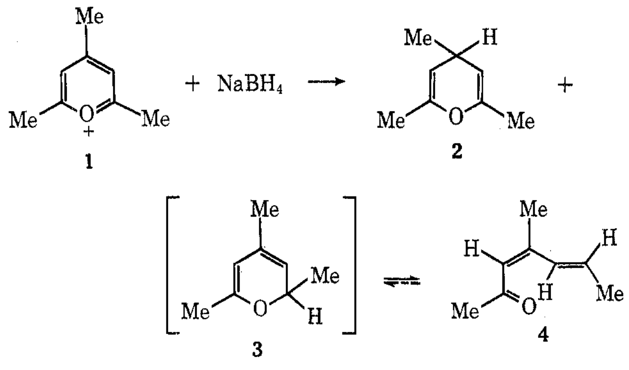
Balaban, Mikai, and Nenitzescu[2] showed that reaction of 2,4,6-trimethylpyryllium perchlorate with sodium borohydride gave two products to which they assigned the structures 2 and 4 (stereochemistry not given). They made the reasonable assumption that 4 was formed by a rapid valence isomerization from 3. Because of our general interest in electrocyclic reactions, we investigated this reaction somewhat more thoroughly than had the previous workers.[2] The reaction proceeds exactly as they described and the two products were isolated in good yield. The nmr spectra are described in the Experimental Section, and these are in accord with the assigned structures. In addition the spectrum of 4 permits us to assign its stereochemistry. Thus the Δ^5 double bond must be trans, since J_{56} is 15.0 Hz, and the Δ^3 double bond is cis since the shift for H_5 (7.63 ppm) can be accounted for only if the acetyl and C_5H groups have a cis orientation.[3]



We were unable to ascertain satisfactorily whether an observable amount of 3 is in equilibrium with 4 or not. The nmr spectrum of 4 has peaks of low intensity at δ 1.18 (d), 4.77, and 4.85 which might be assigned to 3, but these do not exhibit the expected intensity increase and decrease on heating and cooling. Furthermore, there are a number of other small peaks which could not be associated with 3 which also appear in the spectrum.

Next we attempted to determine whether 3 could be identified as a transient intermediate. The presence of a transient intermediate was readily shown by spectral means. If the reduction is carried out under an overlayer of pentane at 0°, a diluted aliquot of the pentane layer has λ_{max} 277 nm, which disappears rapidly at room temperature, leaving the λ_{max} 272 nm of 4. The 277-nm band is quite reasonable for the α-pyran 3, since Hinnen and Dreux[4] have found λ_{max} (CH_3OH) 282 nm for 2,2,4,6-tetramethyl-α-pyran. Additional evidence to support a structural assignment for the intermediate was obtained from the nmr spectrum of a solution obtained by reducing 1 with an underlayer of carbon tetrachloride. At $-22°$ the spectrum shows (in addition to bands due to 2 and 4) resonances at δ 1.18 (d, J = 6.5 Hz), 1.56 (s), 1.76 (s), 4.6 (m), 4.8 (broad s), and 4.9 (broad s). When the solution is warmed to 35°, these bands rapidly disappear and the final spectrum matches that of the crude reduction product obtained from the normal reaction procedure. These data provide strong support for the assignment of structure 3 to the transient intermediate.

An estimate of the rate of conversion of 3 to 4 was obtained by following the change in absorbance at 253.5 nm where the intermediate showed no absorption. With the assumption that 3 goes directly to 4 with no intermediate, the rate of disappearance of 3 can be calculated. The reaction shows good first-order kinetics with k (13°) $\cong 3 \times 10^{-3}$ sec^{-1}. More recently we have shown[5] that the rate of ring opening of 2,2,4,6-tetramethyl-α-pyran is 1.6×10^{-4} sec^{-1} at 14.6°. Since 3 is lacking the cis methyl group on the terminal carbon present in 2,2,4,6-tetramethyl-α-pyran, which is expected to reduce the rate of the latter, the rate difference of *ca.* 20-fold seems quite reasonable.

Experimental Section

2,4,6-Trimethyl-4*H*-pyran (2) and 4-Methyl-*cis*-3-*trans*-5-heptadien-2-one (4).—An aqueous solution of 1 was reduced with sodium borohydride according to the procedure of Balaban, Mikai, and Nenitzescu.[2] The two products were separated by fractional distillation using a Nester and Faust 30-cm spinning band column. The pyran 2, bp 30° (6 mm), nmr (CCl_4) δ 0.98 (d, J = 6.5 Hz, 3 H), 1.71 (d, J = 0.8 Hz, 3 H), 2.79 (m,

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[1] Support of this study by the National Science Foundation under Grant GP-4985 is gratefully acknowledged.

[2] A. T. Balaban, G. Mikai, and C. D. Nenitzescu, *Tetrahedron*, **18**, 257 (1962).

[3] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881, 2886 (1960).

[4] A. Hinnen and J. Dreux, *C. R. Acad. Sci., Ser. C*, **255**, 1747 (1962).

[5] E. N. Marvell, T. Chadwick, G. Caple, T. Gosink, and G. Zimmer, *J. Org. Chem.*, **37**, 2992 (1972).