Tieren sind Ammoniten vorherrschend, und es liess sich eine breite und detaillierte Faunen- und Schichtgliederung durchführen. Die Bedeutung der Gliederung wird im Hinblick auf stratigraphische Zonenbildung und allgemeine Korrelation kurz besprochen. Die Gliederung der Schichtfolgen ist zur Aufklärung der Biologie und Evolution der Ammoniten brauchbar. Von besonderem Interesse erweisen sich die Ammoniten des mittleren und oberen Jura von Grönland, da sie ein klares Beispiel geben für die Tendenz einzelner Familien, sich in ihrer Ausbreitung auf begrenzte Faunengebiete zu beschränken. Die Grenzen solcher Provinzen blieben nicht dieselben und Unterbrechungen in den zu beobachtenden Faunen an bestimmten Stellen sind oft auf Auswanderungen der Faunen zurückzuführen. Unterbrechungen dieser Art dürfen keinesfalls übersehen werden, wenn eine phylogenetische Klassifizierung versucht wird. So haben die ermittelten Schichtfolgen von Grönland einige phylogenetische Ungewissheiten aufklären können.

Brèves communications – Kurze Mitteilungen – Brevi comunicazioni – Brief Reports

The Structure of Ocoteine (Thalicmine)

Ocoteine is an aporphine alkaloid which was isolated from the bark of *Ocotea puberula* Nees[1]. From its degradation products, it was suspected to be identical to thalicmine[2], an alkaloid isolated by YUNUSOV and PROGRESSOV from the bark of *Thalictrum minus* L.[3]. A direct comparison kindly performed by Prof. YUNUSOV confirmed the identity of both alkaloids[4].

Ocoteine has three methoxyls and one methylene dioxygroup. On the basis of the relation to cotarnine, the Russian workers proposed the structure of 5,6-methylenedioxy-3,4,7-trimethoxyaporphine (I)[3]. The partial structure (II) has been put forward to explain the isolation of 4,5-dimethoxy-N-methyl phtalimide (III) by oxidation of the base itself and of *m*-hemipinic acid by permanganate oxidation of the corresponding methylenedioxytrimethoxy-1-methylaminoethyl-9,10-phenanthraquinone[2]. The latter compound was also found in the bark of *Ocotea puberula*[1]. Structure (II) was suggested because no alkaloid was known at the time to have positions 1 and 7 substituted. Positions 2, 3 and 4 are the most commonly substituted besides C-5 and C-6 where all naturally occurring aporphines are substituted by oxygenated substituents.

Dr. S. GOODWIN of the National Institutes of Health (Bethesda) recorded a few years ago the proton resonance spectrum of ocoteine and she interpreted her results in terms of structures (IV) and (V), the former one being preferred[5].

By the courtesy of Dr. N. SHEPPARD (Cambridge University) we were able to record the spectra of several aporphine alkaloids and of ocoteine. When converted to the same units—τ units—our data correspond to those of Dr. S. GOODWIN.

Our results together with the rotatory dispersion curve of ocoteine[6] and the physical data previously published[2] support structure (IV) for ocoteine (thalicmine).

Evidence for structure (IV) is provided by the following facts: (a) the chemical shift data for the aromatic protons collected in the Table together with the N–CH_3 and O–CH_3 absorption values already published elsewhere[7] indi-

Table[a]

Name		Formula			O-CH_3						Aromatic protons			
		R^1	R^2	R^3	2[b]	3[b]	4	5	6[b]	7	1[b]	2[b]	4	7[b]
Dicentrine	VI	OCH_3	H	—	6.20	6.20	—	—	—	—	3.30	—	2.42	3.62
Bulbocapnine	VI	H	OH	—	—	6.20	—	—	—	—	3.25	3.25	—	3.45
o-Methylbulbocapnine	VI	H	OCH_3	—	—	6.18	6.28	—	—	—	3.07	3.07	—	3.32
Corydine	VII	H	OCH_3	—	—	6.18	6.35	—	6.18	—	3.12	3.02	—	3.35
o-Methylcorydine	VII	H	OCH_3	CH_3	—	6.18	6.32	6.37	6.18	—	3.15	3.15	—	3.35
Glaucine	VII	OCH_3	H	CH_3	6.20	6.25	—	6.45	6.20	—	3.42	—	2.00	3.55
Ocoteine (thalicmine)	IV	—	—	—	6.13	6.13	—	—	—	6.07	3.27	—	2.43	—

[a] In τ units.

[b] Assignments of resonance to these positions may be interchanged.

Measurements were made at 40 Mc using a Varian Associates 12″ electromagnet. Calibration of the peaks was made by using side bands generated by a decode oscillator. The substances were examined in chloroform solution and silicon tetramethyl used as an internal standard.

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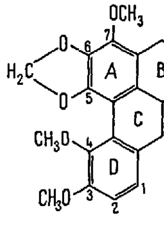
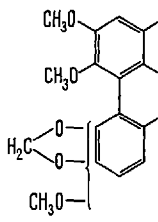


(I)



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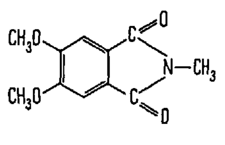

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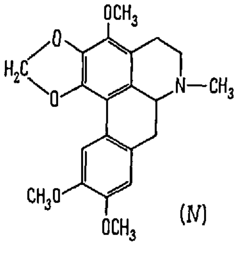
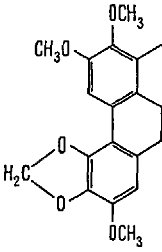


(IV)



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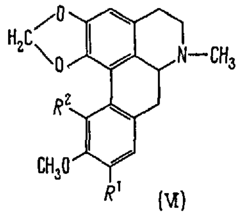

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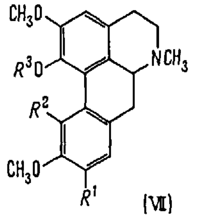
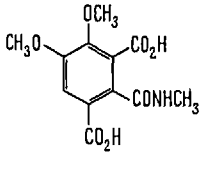


(VII)



(VIII)

cate that either C-4 or C-5 is unsubstituted. Goodwin et al.[8] have pointed out that the aromatic proton at C-4 in dicentrine (VI, $R^1 = O\text{–}CH_3$, $R^2 = H$) absorbs at much lower frequency (2.42 in our data) than found for the remaining aromatic protons. Ocoteine shows a strong absorption at 2.43 indicating that one of the strained positions (C-4 or C-5) of the biphenyl system is unsubstituted. Since all natural aporphines are substituted at both C-5 and C-6, the most probable structure is one like (IV) with C-4 unsubstituted. (b) That C-4 is unsubstituted in ocoteine is confirmed by correlation of its physical properties with the regularities pointed out by Shamma[9]. The presence of a C-4 substituent manifests itself by a high specific rotation at the sodium D line, an ultraviolet absorption maximum near 270 mμ and a relatively lower intensity absorption (log $\varepsilon = 3.6\text{–}4.0$) in the 300 m$\mu$ region, while the C-4 substituted alkaloids show much lower rotations, a bathochromic shift to about 282 mμ and higher absorption around 300 mμ. Ocoteine belongs to the second class since it has been found to exhibit maxima at 283 mμ (log $\varepsilon = 4.25$) and 302 mμ (log $\varepsilon = 4.25$) and it is weakly dextrorotatory (+37.6 in ethanol)[2]. (c) The practical identity to within the experimental error of its rotatory dispersion curve with that of (+) dicentrine[6] favors structure (IV) for ocoteine, which can be considered to be a 7-methoxydicentrine. From a consideration of the specific rotation in different solvents (D line) it was concluded that ocoteine belongs to the (+) glaucine series[2]. Djerassi, Mislow and Shamma found that the sign of the specific rotation at 589 mμ is a true criterion of the absolute configuration of the aporphine bases[10]. Since ocoteine is dextrorotatory at the sodium D line, like (S)(+)dicentrine and (S)(+)glaucine, it must belong to the (S) series. Shamma has also correlated the structures of the aporphine bases with their absolute configuration[11]. If one considers only the substituents on ring D of the aporphines, regardless of the nature of ring A, it is found that certain substituents at particular positions can always be associated with a specific absolute configuration[11]. For instance, the 2,3-dimethoxy combination which is present in glaucine, dicentrine and glaucentrine is always associated with a dextrorotatory base of the (S) series. The fact that ocoteine belongs to this series[2] points to a 2,3-dimethoxy substitution in ring D, leaving position 4 free, confirmed by its low specific rotation at the sodium D line. (d) The remaining methoxyl-group must be located at C-7 because none of the chemical shift values found for the three methoxyl-groups of ocoteine (6.07–6.13–6.13) corresponds to a methoxyl-group in position 5, as can be seen by inspection of the data in the Table. Methoxyl-groups located at that position are pushed out of the aromatic plane by the neighbouring proton or methoxyl at C-4 and hence absorb at higher fields (6.37 in O-methylcorydine and 6.45 in glaucine)[7].

Furthermore, structure (IV) explains a basic fact about the chemistry of ocoteine, since on oxidation it gives *m*-hemipinic acid methylimide (III). Structure (V) would give *m*-hemipinic acid methylimide (III) if decarboxylation occurred next to the methoxyl-group in an intermediate such as (VIII)[5]. Previous experience from our laboratory indicates that tricarboxylic acids derived from ring A of aporphines are fairly stable and that decarboxylation, although not impossible, does not take place easily during that reaction[2,12].

In the nuclear magnetic resonance spectrum of ocoteine (at 60 Mc), Goodwin has also observed[5] a quartet of lines corresponding to a small chemical shift between the two hydrogen atoms of the methylenedioxy-ring[8]. In our spectrum—recorded at 40 Mc—a broad doublet at $\tau = 4.1\text{–}4.2$ appears, suggesting an incipient splitting caused by the non-equivalence of the two hydrogen atoms due to a non-planarity of the linked biphenyl system[9,13].

Résumé. Par l'étude du spectre de résonance magnétique nucléaire et par la considération de sa rotation optique de sa dispersion rotatoire et des spectres de l'ultraviolet, on propose la formule (IV) pour la ocotéine (thalicmine).

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