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Review

^{13}C NMR spectroscopy of tri- and tetracyclic quinolizidine alkaloids. Compilation and discussion

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ABSTRACT: A comprehensive collection of ^{13}C chemical shifts of 159 tri- and tetracyclic quinolizidine alkaloids (sparteine derivatives) is presented. The data are discussed in terms of substituent effects, molecular geometries and protonation effects. Some IR, ^{1}H and ^{15}N NMR and MS data are included. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{13}C NMR; tri- and tetracyclic quinolizidine alkaloids; stereochemistry; free bases and salts; substituent effects; steric effects; protonation effects

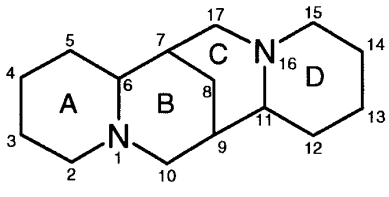
INTRODUCTION

Many representatives of tri- and tetracyclic quinolizidine (lupine) alkaloids (Scheme 1) are naturally occurring compounds isolated from *Leguminosae* plants.[1] Some of them have been used in folk medicine of Eastern Asia and are nowadays of medical interest because of their oxytoxic and antiarrhythmic (sparteine, lupanine), hypoglycemic (lupanine), hallucinogenic (cytisine, *N*-methylcytisine), teratogenic (anagyrine) and inhibitory effects of natural killer cell growth.[2]

Many publications have appeared in the last few years reporting the use of sparteine as a very efficient chiral diamine, demonstrating promising potential for asymmetric transformations of organometallic reagents to achieve enantioselective deprotonation, polymerization and carbonyl addition reactions.[3]

STEREOCHEMISTRY

The skeleton of sparteine and its derivatives may be considered as two fused quinolizidine rings. The absolute configurations of the three main alkaloid skeletons are as follows: 6*R*, 11*S* for (−)-sparteine (Scheme 2), 6*R*, 11*R* for (−)-α-isosparteine (Scheme 3) and 6*R*, 11*R* for (+)-β-isosparteine (Scheme 4).[1c,d]



Scheme 1. General structure and atom numbering of tetracyclic alkaloids.

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There are two possible conformation-changing processes which occur in solution and may allow interconversion between different conformations: nitrogen and ring inversion.

The *trans* connection of A/B rings in the sparteine molecule is rigid whereas that of C/D rings is labile, and it can exist in a *cis* chair–chair or *trans* boat–chair conformational equilibrium. Sparteine and its derivatives have been studied by IR,[4,5] ^{1}H NMR[5,6] and ^{13}C NMR spectroscopy[7] and it has been shown that the free bases exist predominantly in A/B *trans* chair–chair and C/D *trans* boat–chair conformations (Scheme 2). In the monosalts of sparteine a hydrogen bond stabilizes the all-chair A/B *trans* and C/D *cis* conformations.[8] There is no such possibility in the diprotonated form. Therefore, the conformation of the dications in solution resembles that of the free bases.[9]

The conformation of the rings in α-isosparteine is the same in the free base and in mono- and disalts,[10] namely *trans–trans*, all-chair (Scheme 3).

There is some controversy about the conformational behaviour of β-isosparteine in solution. On the basis of IR spectra it has been assumed that the compound exists in another conformation, *cis*-A/B chair–chair and *cis*-C/D boat–chair forms.[11] Later, with the help of ^{13}C NMR spectra,[12] it was demonstrated that a dynamic equilibrium is present with a predominance of the symmetrical A/B chair–boat and C/D boat–chair conformations in chloroform solution at room temperature. That implies again nitrogen inversion and a change in the ring junction from *cis* to *trans*. ^{13}C NMR spectra also lead to the conclusion that the monoprotonated form exists as a symmetrical all-chair conformation of the *cis*-quinolizidine rings whereas the diprotonated form consists of a *cis*-quinolizidine ring A/B linked to a *trans*-quinolizidine ring C/D with a boat conformation of ring C (Scheme 4).[10]

Sometimes an oxo group may cause differences in conformation compared with the parent compound. For example, 10-oxosparteine (aphylline) exists in an all-chair *trans*-A/B and *cis*-C/D conformation in solu-

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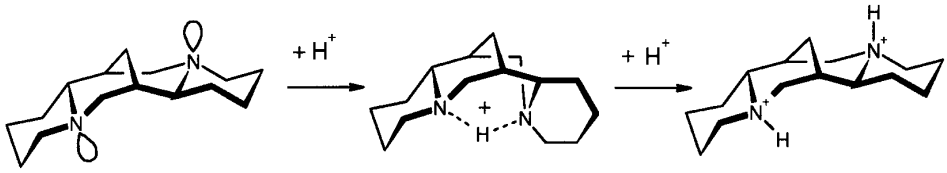
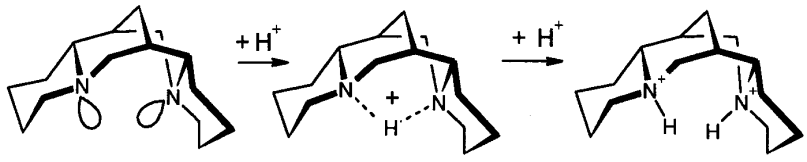
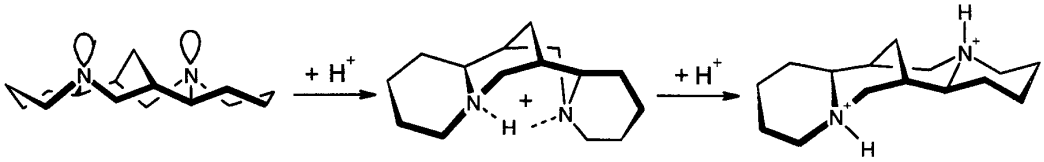


Scheme 2. Sparteine conformations.



Scheme 3. α-Isosparteine conformations.

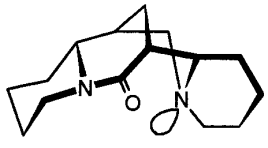


Scheme 4. β-Isosparteine conformations.

tion (Scheme 5). It is assumed that the absence of an *endo*-oriented lone-pair at N-1 allows N-16 to invert in order to avoid the unfavourable boat conformation of ring C.[11,13]

IR SPECTRA

In 1957, Bohlmann[14] reported a criterion for the stereochemical differentiation of the quinolizidine ring fusion. The CH stretching frequency in compounds containing at least two C—H bonds *trans*-axial to the electron lone-pair at the nitrogen atom is lowered to 2800–2700 cm^{-1} owing to specific interactions (most probably hyperconjugation between the nitrogen lone-pair orbital and antibonding orbitals of adjacent C—H bonds). In lactams the lone-pair is involved in conjugation with the oxygen and in oxides in a covalent bond. In these two cases the Bohlmann bands do not appear. The same is observed with substances containing double bonds at the ring junction because of a deformation of the coplanar *trans*-diaxial disposition. The shape, the intensity and the conditions for Bohlmann bands to appear were studied by Skolik and co-workers[4,5,11,15,16] in sparteine, α- and β-isosparteine and their lactames, oxides, deuterated analogues and some salts. It was shown that only one *trans*-axial bond is sufficient. It has been concluded that the general complexity, the fine structure and the integral intensity of the 2840–2600 cm^{-1} absorption region can provide valuable information about the conformation of quinolizidine alkaloids.[4,5,15] However, a more detailed study of the problem is needed, especially for compounds containing substituents, which may influence the conformation of the rings and disturb the needed *trans*-diaxial configuration.



Scheme 5. Conformation of 10-oxosparteine (aphylline).

In Fig. 1, the IR spectra of the stereoisomeric compounds thermopsine (**A**) and anagyrine (**B**) (Scheme 6) illustrate the use of the Bohlmann bands for stereochemical studies of quinolizidine derivatives.[17] There is a clear and pronounced difference in the appearance of the spectral region between 2850 and 2700 cm^{-1} indi-

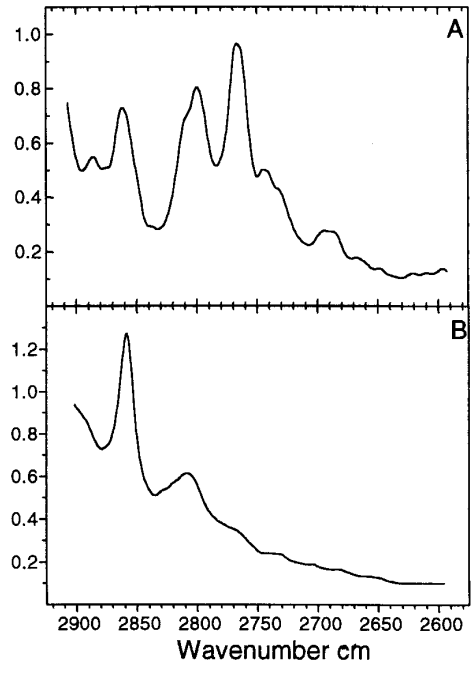
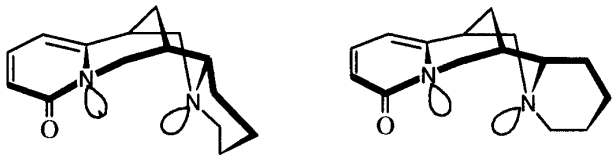


Figure 1. IR spectra of (A) thermopsine and (B) anagyrine.[17]



A B

Scheme 6. Conformations of (A) chermopsine and (B) anagyrine.

cating that **A** has a *trans*- (three *trans*-axial hydrogens) and **B** a *cis*- (only one *trans*-axial hydrogen) junction of the rings C and D.

^{1}H NMR SPECTRA

There have been only a few investigations using ^{1}H NMR spectroscopy for structural and stereochemical analyses of sparteine alkaloids, because most of the signals occur in a narrow region between $\delta = 1.0$ and 3.0 and their overlap is severe. Using partially deuterated compounds, Bohlmann *et al.*[6] assigned the signals of H-2, H-8, H-10, H-15 and H-17 and made conclusions about the stereochemistry of sparteine (ring C in a boat conformation) and β-isosparteine (all rings in chair conformation). Later, the results for sparteine were confirmed by Sadykov *et al.*[18] by homonuclear INDOR experiments. Bohlmann and Schumann[19] investigated the influence of the lactam group on the neighbour protons using quinolizidine as a model and assigned the ^{1}H NMR spectra of some lactams. Wiewiorowski *et al.*[5] also drew conclusions about the stereochemistry of quinolizidine alkaloids. Krueger and Skolik[20] studied the spectra of sparteine- and α-isosparteine-*N*-oxides. In 1986, Golebiewski[21] made a complete assignment of the ^{1}H NMR spectra of sparteine and its lactams via homocorrelated and *J*-resolved 2D spectra and double resonance experiments. The results provided information on the conformation of the rings. A complete ^{1}H signal assignment of two α-isosparteine salts was obtained through two-dimensional phase-sensitive homo- and heteronuclear shift correlation methods, in addition to homo- and heteronuclear relayed coherence transfer, COLOC and NOESY experiments.[22]

The signals of the protons H-9 and the two H-10 can indicate the conformation of ring B. When it is in boat conformation as in β-isosparteine, H-9 and H-10b are in eclipsed position that corresponds to $^{3}J(9,10\alpha)$ and $^{3}J(9,10\beta)$ about 3.0 and 11.0 Hz, respectively. The chair conformation (sparteine, α-isosparteine) of the ring is connected with a *gauche* position of H-9 and the two H-10 and two small vicinal coupling constants (about 2.0 Hz). Similarly, the signals of H-7 and the two H-17 give information about the conformation of ring C. The boat conformation (sparteine, β-isosparteine) is connected with a small and a large vicinal coupling constant and the chair conformation (α-isosparteine) with two small constants. That is why the form of the above mentioned signals can be an unambiguous test for the stereochemistry of tri- and tetracyclic quinolizidine alkaloids.

However, unless an oxo group (as in lupanine) or another substituent is present to deshield the signals of interest, they are buried in an unresolved group. The NMR techniques using selective pulses[23] for one-dimensional analogues of the 2D spectra can help in this case and enhance the use of the ^{1}H NMR in the analysis of the saturated alkaloid systems.

^{15}N NMR SPECTRA

The presence of a free electron pair and its orientation influence ^{15}N chemical shifts and the steric γ-effects work in a similar manner as for the ^{13}C nuclei.[24] Fanso-Fee *et al.*[25] measured the ^{15}N NMR spectra of several indole alkaloids and model compounds. Their experiments demonstrated that a *cis*-fused quinolizidine nitrogen is shielded by 13–15 ppm with regard to the *trans*-fused compound. An explanation similar to that of IR Bohlmann bands was proposed, namely hyperconjugation between the lone electron pair and the s-orbitals of the *trans*-axial CH bonds. Shielding of the *cis*-fused nitrogen atom may reflect an inhibition of this effect because fewer antiperiplanar C—H orbitals are available. The 0.5 ppm difference in resonance positions of the two ^{15}N signals in the spectrum of sparteine (48.6 and 49.1, unassigned) shows that the two nitrogens are in similar environments typical for the *trans*-quinolizidine system and gives a further proof for the *trans* fusion of the rings. The protonation effect in some of the compounds has also been studied. One of the factors expected to influence the magnitudes of protonation shifts is the extent of the lone-pair interaction with adjacent orbitals, via either conjugative or hyperconjugative mechanisms. Hence, nitrogen nuclei whose lone-pair orbitals are hyperconjugatively delocalized would be expected to be deshielded upon protonation to a lesser extent than those whose lone-pairs are localized. Protonation of 3-equatorial- and 3-axial-methyl-*trans*-quinolizidine deshields the ^{15}N nuclei only slightly, and may even be obscured by solvent effects.

In a later investigation reported by Liu *et al.*,[26] the spectra of four quinolizidine derivatives were recorded (anagyrine, thermopsine, 13β-hydroxythermopsine and cytisine), and it was shown that N-16 of the first compound resonated at $\delta = 33.2$, associated with a shielding of *ca.* 19 ppm as compared to the other three compounds. It was proposed that in anagyrine the fusion of the C/D rings is *cis* whereas in the stereoisomeric thermopsine it is *trans*. The results are in accordance with the IR spectra of the substances (see above).

MASS SPECTRA

Mass spectra of the lupine alkaloids are useful for determination of the molecular mass because in most cases

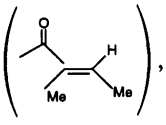
the molecular ions of them are detectable using the electron ionization (EI) technique.[1] However, there is no generalized conclusion to be drawn.

CHEMICAL STRUCTURES AND ^{13}C CHEMICAL SHIFTS OF QUINOLIZIDINE ALKALOIDS, BASES AND PROTONATED COMPOUNDS

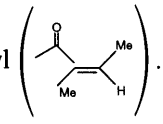
The main tasks in the interpretation of quinolizidine alkaloid spectra are to predict the stereochemistry of the skeleton and the geometric and steric positions of the substituents in addition to the presence of double bonds. For protonated compounds it is important to determine the changes in their stereochemistry in comparison with that of the corresponding free salts.

Table 1 presents the chemical structures and Tables 2 and 3 the ^{13}C chemical shifts of the free bases and protonated quinolizidine alkaloids, respectively. The literature has been covered up to spring 1997.

The letter in the compound abbreviation indicates the basic structure, and the number in front of the hyphen denotes the position of the oxo-group in the ring. The following abbreviations are used for substituents: Me = methyl, Et = ethyl, Pr^i = isopropyl, Pr^n = *n*-propyl, Ac = acetyl, Ph = phenyl,

Tig = tigloyl  ,

and

Ang = angeloyl  .

In some cases we considered it necessary and possible to check the literature data. The first case is the ^{13}C NMR spectrum of lupanine (A2-1) where the assignments of C-7 and C-9 are ambiguous and are often interchanged. We performed ^1H–^1H correlation (COSY-DQF) and heteronuclear inverse correlation (HMQC) experiments on a sample of lupanine. A starting point was the signal of H-10α, according to its clearly defined position at $\delta = 4.5$ due to the anisotropic effect of the lactam group. The signals of C-7 and C-9 are assigned to be at $\delta = 32.4$ and 34.9, respectively. This is in accordance with the correction of the original assignment of these signals for sparteine made by Shaka and Freeman[27] on the basis of INADEQUATE and selective heteronuclear polarization transfer experiments.

The second case was the inspection of the stereoisomeric compounds anagyrine (D-1) and thermopsine (D-2). The form of the signals of the two H-10 [$^3J(10\alpha,9) \approx 7$ Hz, $^3J(10\beta,9) \approx 1$ Hz) and H-7 (an unresolved singlet), being an indication for flattened boat of B (sofa) and chair of C in both substances (see ^1H NMR Spectra section), conflicts with the stereochemistry proposed in Ref.[26]: rings B in chair and C in boat conformation. In addition, different sets of ^{13}C spectral data for anagyrine have been published.[26,28,29] Therefore, we performed COSY-DQF, HMQC and NOE spectra on samples of anagyrine and thermopsine isolated from *Thermopsis mongolica*.[30] The observed NOE effects gave further information about the relative configurations of anagyrine and thermopsine. An enhancement was observed for H-11 in anagyrine and for H-12α in thermopsine upon irradiation of H-10α. Hence the configurations were determined to be 7*S*,9*S*,11*S* and 7*S*,9*S*,11*R* for anagyrine and thermopsine, respectively (or their mirror images 7*R*,9*R*,11*R* and 7*R*,9*R*,11*S*).

The ^{13}C chemical shifts of D-1 and D-2 assigned via inversed heterocorrelation experiments are given in Table 3.

DISCUSSION

Substituent effects on the ^{13}C chemical shifts

The knowledge of the substituent effects has been helpful in the assignment of the ^{13}C signals since the earliest years of the development of ^{13}C NMR spectroscopy.[70] The reason is the additivity and reproducibility of the effects for related compounds and also the pronounced stereochemical dependence. Although the 1D and 2D NMR techniques now permit the interpretation of even the most complicated and overlapping spectra, the creation of additivity schemes and suitable increments for calculating ^{13}C chemical shifts of unknown compounds is still under active study. The reason is the simplicity of the method and its ability to be used by groups not equipped with modern NMR spectrometers. This approach can be especially helpful for six-membered cyclic compounds because of the clearly defined position of the substituents (axial or equatorial). The data published for cyclodecalols[71] prove that the same is also valid for fused six-membered carbocycles. It has been shown that a linear correlation exists between the chemical shifts for methyl-substituted decalins and quinolizidines.[72]

Table 4 illustrates the substituent effects and Table 5 the effects of oxo groups on the ^{13}C chemical shifts calculated as the difference in the chemical shifts of the substituted and unsubstituted compounds.

The comparison of the chemical shifts of 2-methylsparteine with the corresponding 4-methylquinolizidine and of 6-methylsparteine and 6-α-isosparteine with their corresponding 10-methylquinolizidine[72] reveals similar substituent effects for all three types of compounds, which reflect the similarity in the stereochemistry.

From the calculated substituent effects (Table 4) it can be seen that, as in cyclohexanols and specially in decalols,[71] the α-effects of the equatorial hydroxyl groups are larger than those of the axial groups. A similarity is not found with the β-effects reported in Table 4. The effects of equatorial hydroxy substituents in decalols are consistently larger than those for their axial

Table 1. Chemical structures[a]

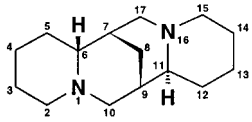
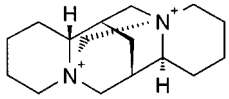
	Structure	Name	Ref.
			
A-1	—	(−)-Sparteine	7[b], 27, 28
$(A\text{-}1)^{+}\cdot ClO_4^{-}$			8, 10
$(A\text{-}1)^{2+}\cdot 2ClO_4^{-}$			9
$(A\text{-}2)^{+}\cdot I^{-}$	N(1)-Me		12
$(A\text{-}3)^{2+}\cdot 2I^{-}$			12
A-4	2α-Me (e)		7
$(A\text{-}4)^{+}\cdot ClO_4^{-}$			8
A-5	2β-CN (a)		31
A-6	2α-Ph (e)		7
$(A\text{-}6)^{+}\cdot ClO_4^{-}$			8
A-7	6β-Me (a)		32, 33
$(A\text{-}7)^{2+}\cdot 2ClO_4^{-}$			33
A-8	6β-Et (a)		32
A-9	8-*anti*-OH (e)		28
A-10	9β-OH (e)		34
A-11	10α-CH_2OH (e)		35
A-12	12α-OH (e)	Retamine	28, 36
A-13	13α-OH (a)		28
A-14	13α-OAc (a)		28
A-15	15β-Ph (e)		7
$(A\text{-}15)^{+}\cdot ClO_4^{-}$			8
$(A\text{-}16)^{+}\cdot I^{-}$	N(16)-Me		12
A-17	17β-Me (e)		32
A-18	17β-Et (e)		32
A-19	2α-Me (e), 2β-CN (a)		7
$(A\text{-}19)^{+}\cdot ClO_4^{-}$			8
A-20	2-CN, 2-Ph		7
$(A\text{-}20)^{+}\cdot ClO_4^{-}$			8
A-21	2-CN, 2-Tolyl		7
A-22	2-Ph, 17-Pr^{ic}		7
$(A\text{-}23)^{+}\cdot ClO_4^{-}$	N(1),6-Dehydro		37
$(A\text{-}23)^{2+}\cdot 2ClO_4^{-}$			13
A-24	2,3-Didehydro		31
A-25	2,3-Dehydro, 2-Me		7
$(A\text{-}25)^{2+}\cdot 2ClO_4^{-}$	N(1),2-Dehydro, 2-Me		9
A-26	2,3-Dehydro, 2-Ph		7
$(A\text{-}26)^{2+}\cdot 2ClO_4^{-}$	N(1),2-Dehydro, 2-Ph		9
$(A\text{-}26)^{2+}\cdot 2Cl^{-}$	N(1),2-Dehydro, 2-Ph		9
$(A\text{-}26)^{2+}\cdot 2Br^{-}$	N(1),2-Dehydro, 2-Ph		9
A-27	2,3-Dehydro, 2α-Tolyl (e)		7
$(A\text{-}27)^{2+}\cdot 2Cl^{-}$	N(1),2-Dehydro, 2-Tolyl		9
A-28	2,3-Dehydro, 2-Ph, 17-Pr^{i}		7
A-29	2,3-Dehydro, 4α-OH (a), 4β-Me (e)		38
A-30	14,15-Dehydro, 15-Ph		7
$(A\text{-}30)^{+}\cdot ClO_4^{-}$			8
$(A\text{-}30)^{2+}\cdot 2Cl^{-}$	N(16),15-Dehydro, 15-Ph,		9
$(A\text{-}31)^{2+}\cdot 2ClO_4^{-}$	N(1),6-Dehydro, N(16),11-dehydro		39
A2-1	2-Oxo	Lupanine	28, 40
A2-2	2-Oxo, 3α-OH (a)		41, 42
A2-3	2-Oxo, 3α-OAc (a)		42
A2-4	2-Oxo, 3β-OH (e)		43
A2-5	2-Oxo, 6β-OH (a)		44, 45
A2-6	2-Oxo, 12α-OH (e)		36
A2-7	2-Oxo, 13α-OH (a)		28, 46, 47

Table 1—*Continued*

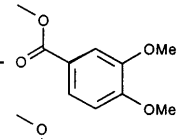
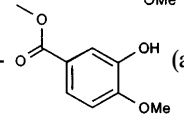
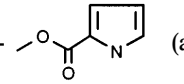
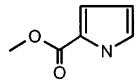
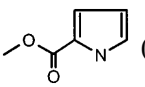
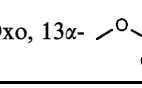
	Structure	Name	Ref.
A2-8	2-Oxo, 13α-OTig[c] (a)		48
A2-9	2-Oxo, 13α-O(2-Methylbutyryl) (a)		48
A2-10	2-Oxo, 13α-OAng[c] (a)		48
A2-11	2-Oxo, 13α-O(4′-OH-Tig) (a)		49
A2-12	2-Oxo, 13α-O(3′-OH-*cis*-oct-5-enoyl) (a)	Cineroctine	47
A2-13	2-Oxo, 13α-  (a)	Cinevanine	48
A2-14	2-Oxo, 13α-  (a)	Cineverine	47
A2-15	2-Oxo, 13α-  (a)	Calpurnine	46
A2-16	2-Oxo, 13β-OH (e)		28, 47
A2-17	2-Oxo, N(16)-O		50
$(A2\text{-}18)^+ \cdot I^-$	2-Oxo, N(16)-Me		13
A2-19	2-Oxo, 3β-OH (e), 4α-OH (e)	Lebeckianine	51
A2-20	2-Oxo, 3β-OH (e), 4α-OAng (e)	Sessilifoline	43
A2-21	2-Oxo, 3β-OH (e), 13α-OH (a)		52
A2-22	2-Oxo, 3β-OH (e), 13α-OAng (a)	Cajanifoline	43
A2-23	2-Oxo, 3β-OH (e), 13α-OTig (a)		53
A2-24	2-Oxo, 8-*anti*-OH (e), 13α-OH (a)		54
A2-25	2-Oxo, 8-*anti*-OH (e), 13α-OAng (a)	Cryptanthine	43
A2-26	2-Oxo, 12β-OH (a), 13α-OH (a)	Calpurmenine	46
A2-27	2-Oxo, 12β-OH (a), 13α-  (a)		46
A2-28	2-Oxo, 3β-OH (e), 4α-OH (e), 13α-OH (a)		46
A2-29	2-Oxo, 3β-OH (e), 4α-OH (e), 13α-  (a)	Calpaurine	46, 55
A2-30	2-Oxo, 3β-OH (e), 8-*anti*-OH (e), 13α-OH (a)		54
A2-31	2-Oxo, 3β-OH (e), 8-*anti*-OH (e), 13α-OAng (a)		54
A2-32	2-Oxo, 5,6-Dehydro		44, 56
$(A2\text{-}33)^+ \cdot ClO_4^-$	2-Oxo, N(16), 11-Dehydro		12
$(A2\text{-}34)^+ \cdot ClO_4$	2-Oxo, N(16), 17-Dehydro		13
A4-1	4-Oxo, 3β-Me (a)		38
A4-2	4-Oxo, 2,3-Dehydro	Multiflorine	57, 58, 59 60
$(A4\text{-}2)^+ \cdot ClO_4^-$			58, 60
A4-3	4-Oxo, 2,3-Dehydro, N(16)-Oxide		59
A4-4	4-Oxo, 2,3-Dehydro, 13α-OH		57, 58
$(A4\text{-}4)^+ \cdot ClO_4^-$			58
A4-5	4-Oxo, 2,3-Dehydro, 5,6-Dehydro		57, 58
A4-6	4-Oxo, 2,3-Dehydro, 5,6-Dehydro, 13α-OH (a)		58
A8-1	8-Oxo		28
A10-1	10-Oxo	Aphylline	13
A10-2	10-Oxo, 13α-OH (a)	Virgiline	46
A10-3	10-Oxo, 13α-  (a)		46

Table 1—*Continued*

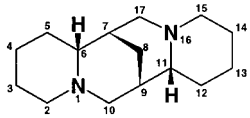
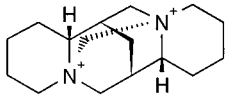
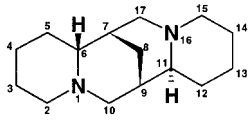
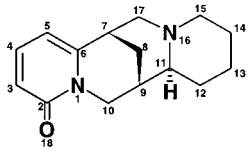
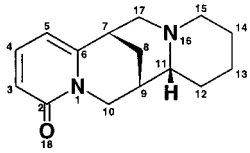
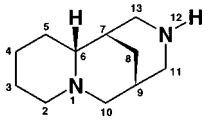
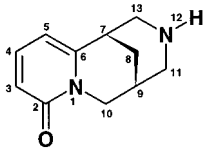
	Structure	Name	Ref.
A10-4	10-Oxo, 5,6-Dehydro	Aphyllidine	34
A10-5	10-Oxo, 5,6-Dehydro, 2α-OH (e)	Argyrolobine	34
A10-6	10-Oxo, 5,6-Dehydro, 2α-OAc (e)		34
A10-7	10-Oxo, 5,6-Dehydro, 3β-OH (e), 9β-OH (e)		34
A10-8	10-Oxo, 5,6-Dehydro, 3β-OAc (e), 9β-OAc (e)		34
A10-9	10-Oxo, 5,6-Dehydro, 3α-OAc (a), 9β-OAc (e)		34
A15-1	15-Oxo		32, 40
A15-2	15-Oxo, 6β-Me (a)		32
$(A15\text{-}3)^+ \cdot I^-$	15-Oxo, N(1),6-Dehydro		13
A17-1	17-Oxo		32, 40
$(A17\text{-}2)^+ \cdot I^-$	17-Oxo, N(1)-Me		13
A17-3	17-Oxo, 6β-Me (a)		32
A17-4	17-Oxo, 6β-Et (a)		32
A17-5	17-Oxo, 6β-Pr^n (a)		32
$(A17\text{-}6)^+ \cdot ClO_4^-$	17-Oxo, N(1),6-Dehydro		13
A2,17-1	2-Oxo, 17-Oxo		40, 61
A2,17-2	2-Oxo, 17-Oxo, 15β-OH (e)		61
A13,17-1	13-Oxo, 17-Oxo		28
			
B-1	–	(−)-α-Isosparteine	7, 28, 32
$(B\text{-}1)^+ \cdot ClO_4^-$	–		10
$(B\text{-}1)^{2+} \cdot 2C1O_4^-$	–		10
$(B\text{-}2)^+ \cdot I^-$	N(1)-Me		22
$(B\text{-}3)^{2+} \cdot 2I^-$			22
B-4	6β-Me (a)		32
B-5	9β-OH (e)		28
B-6	6β-Me (a), 11β-Me (a)		32
B2-1	2-Oxo	Isolupanine	28, 42
B2-2	2-Oxo, 13-βOH (e)		28
B17-1	17-Oxo		28
B10,17-1	10-Oxo, 17-Oxo		28
			
C-1	–	(+)-β-Isosparteine	12
$(C\text{-}1)^+ \cdot ClO_4^-$			10
$(C\text{-}1)^{2+} \cdot 2ClO_4^-$			10
C17-1	17-Oxo		12
$(C17\text{-}1)^+ \cdot ClO_4^-$			12
D-1		(+)-Anagyrine	26, 28, 29, 62
D-2		Thermopsine	26, *62*

Table 1—*Continued*

	Structure	Name	Ref.
D-3	13β-OH (e)		26
			
E-1	N(12)-Me		63
E-2	8-*anti*-OH, N(12)-Me		63
E-3	8-*syn*-OH, N(12)-Me		63
E-4	8-*anti*-$OCOC_6H_4Cl$(p) (e), N(12)-Me		63
E-5	8-*syn*-$OCOC_6H_4Cl$(p) (a), N(12)-Me		63
E2-1	2-Oxo, 11β-$CH_2CH{=}CH_2$ (a)	Angustifoline	49, 64
E2-2	2-Oxo, 11β-$CH_2CH{=}CH_2$ (a), N(12)-CHO		65
E2-3	2-Oxo, 11β-$CH_2CH{=}CH_2$ (a), N(12)-CO-O-Me		65
E2-4	2-Oxo, 11β-$CH_2CH{=}CH_2$ (a), N(12)-$COOCH_2Me$		65
E4-1	4-Oxo, 2,3-Dehydro N(12)-$CH_2CH_2CH{=}CH$		57
$(E4\text{-}1)^+ \cdot ClO_4^-$			60
E4-2	4-Oxo, 2,3-Dehydro, 13β-$CH_2CH{=}CH$ (a), NH (a)	Albine	57
$(E4\text{-}2)^+ \cdot ClO_4^-$			57
E4-3	4-Oxo, 2,3-Dehydro, 13β-$CH_2CH{=}CH$ (a), NH (e)		57
E4-4	4-Oxo, 2,3-Dehydro, 5,6-Dehydro, 13β-$CH_2CH{=}CH$ (a), NH (a)		57
E4-5	4-Oxo, 2,3-Dehydro, 5,6-Dehydro, 13β-$CH_2CH{=}CH$ (a), NH (e)		57
E8-1	8-Oxo, 10-Ph		63
E8-2	8-Oxo, N(12)-Me		63
E10-1	10-Oxo	Virgilidone	66
			
F-1	—	Cytisine	28, 44, 67
F-2	11α-CH_2-$CH{=}CH_2$ (e)		44
F-3	N(12)-Me		44, 68
F-4	N(12)-OH		67
F-5	N(12)-CH_2CONH_2		67
F11-1	11-Oxo	11-Oxocytisine	69

[a] Stereochemistry given if known; a = axial, e = equatorial.
[b] The values of the chemical shifts are taken from the underlined reference.
[c] For abbreviations, see text.

Table 2. ^{13}C chemical shifts δ (ppm) of the free bases

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-17	S[a]	Substituent signals
A-1[b]	56.0	25.6	24.5	29.1	66.3	32.9	27.4	35.9	61.8	64.2	34.5	24.5	25.8	55.2	53.4	C	
A-4	58.0	35.3	24.5	30.2	66.2	33.8	27.5	36.4	57.3	64.4	34.7	24.9	26.0	55.3	53.5	C	21.3
A-5	55.3	20.3	25.7[c]	28.5	60.4	32.5	28.1	35.6	59.2	64.6	34.3	24.8[c]	26.7	55.6	53.3	C	117.2
A-6	69.3	37.0	24.6	30.0	66.9	33.8	27.0	36.2	58.6	64.5	34.5	24.9	25.8	55.7	53.7	C	126.5, 127.4, 128.3, 146.0
A-7	49.6	26.2	20.3	33.2	55.4	38.5	20.6	36.2	55.7	65.2	34.4	24.8	25.9	55.5	54.1	C	10.9
A-8	48.8	27.5	20.1	30.2	57.3	36.1	20.1	31.7	55.7	63.9	34.3	24.9	26.2	55.3	54.1	C	8.1, 12.7
A-9	55.2	25.8	24.5	29.8	64.6	40.4[e]	73.9	43.2[e]	60.3	63.6	36.0	24.5	26.1	54.9	52.9	C	
A-10	56.0	25.6	24.6	28.6	65.4	33.7	36.5[c]	69.0	68.8	68.3	26.3[c]	24.8	25.3	55.7	53.1	C	
A-11	52.6	25.6	23.0	29.1	66.4	35.1	26.6	37.4	66.2	65.0	31.9	23.4	24.3	55.6	59.9	P	62.0
A-12	56.2	25.8	24.6	29.3[c]	66.4	32.7	28.8[c]	33.0	62.2	66.9	70.9	31.3	19.9	54.8	52.8	C	
A-13	56.2	25.7	24.7	29.3	66.5	33.1[e]	27.4	35.6[e]	61.7	57.2	41.7	64.6	32.8	49.2	53.2	C	
A-14	56.3	26.0	24.8	29.5	66.5	33.3[e]	27.4	35.7[e]	61.9	58.3	38.4	68.8	29.5	49.8	53.1	C	
A-15	56.3	25.8	25.1	29.3	66.6	33.4	27.7	36.8	61.7	64.0	34.0	24.7	35.8	68.9	49.9	C	126.5, 127.5, 128.2, 145.9
A-17	56.3	25.9	24.8	29.2	66.5	43.2	27.3	37.0	61.7	64.7	35.3	25.3	26.3	52.0	56.8	C	22.9
A-18	56.5	25.9	24.9	29.4	66.6	39.9	27.7	36.9	61.9	64.0	35.5	25.4	26.5	51.7	60.5	C	7.7, 27.7
A-19	58.2	38.3	21.1	29.9	61.6	33.1	26.7	35.8	53.7	64.5	34.2	24.7	25.6	55.3	53.2	C	26.5, 119.1
A-20	68.9	41.6	21.7	29.0	62.0	34.8	27.1	35.9	54.9	64.4	33.7	25.0	25.8	55.9	53.7	C	117.3, 126.0, 128.3, 128.7, 140.8
A-21	68.8	41.6	21.7	29.0	62.0	33.6	27.1	35.9	54.8	64.5	34.2	25.0	25.7	55.6	53.6	C	117.4, 21.0, 126.9, 129.4, 137.9, 138.1
A-22	69.4	37.0	24.9	31.0	66.8	34.8	28.3	37.0	59.1	63.4	36.2	25.9	27.1	52.5	63.7	C	126.5, 127.4, 128.2, 146.1, 15.4, 19.9, 28.9
A-24	138.4	97.8	22.2	26.7	60.3	32.7	27.6	36.5	58.1	64.2	35.0	25.4	26.4	55.7	53.2	B	
A-25	142.2	97.2	22.3	27.1	61.0	32.8	27.2	36.0	52.8	64.2	34.5	24.9	25.8	55.4	53.0	C	20.6
A-26	149.3	102.2	22.8	26.9	62.3	33.0	27.8	36.2	54.8	64.3	34.3	25.0	25.9	55.7	52.9	C	126.0, 127.8, 140.0
A-27	148.9	101.6	22.9	27.0	62.4	33.2	27.8	36.4	54.8	64.3	34.0	25.1	26.0	55.7	52.9	C	21.1, 127.8, 128.5, 136.2, 137.5
A-28	149.3	102.7	23.1	27.8	63.6	33.9	28.9	37.0	55.3	63.0	36.0	25.9	27.0	52.0	63.3	C	126.7, 127.8, 140.5, 15.1, 19.9, 28.3
A-29	137.6	105.7	68.5	42.7	59.7	31.7	27.1	35.5	57.4	64.3	34.4	24.8	25.7	55.2	52.7	C	32.9
A-30	57.3	25.4	25.2	29.6	66.4	35.0	26.3	35.7	62.9	60.2	30.4	23.8	107.4	149.1	46.9	C	127.1, 127.5, 127.8, 140.0
A2-1	171.4	33.1	19.7	26.8	61.0	32.4	27.5	34.9	46.8	64.2	33.5	24.5	25.2	55.6	52.9	C	
A2-2	172.1	67.5	26.7	22.4	59.3	33.7	26.9	34.3	47.2	63.2	31.5	23.8	24.5	54.8	51.3	C	
A2-3	166.9	70.0	25.4	21.6	60.3	32.9	26.6	34.9	47.2	63.5	33.2	24.4	25.0	55.3	52.1	C	21.6, 169.9
A2-4	173.6	67.9	26.2[c]	24.4[c]	61.5	34.4[e]	27.1	32.1[e]	47.7	64.0	33.2	24.2	25.0	55.3	52.7	C	
A2-5	172.0	33.2	19.2	32.2	85.5	37.5	15.9	34.3	42.5	64.3	34.2	24.1	24.1	55.3	54.1	C	
A2-6	171.5	33.0	19.5	27.3	61.0	31.9	27.9	32.1	47.0	66.7	70.6	30.9	19.8	55.0	52.5	C	
A2-7	171.9	32.4	18.9	26.8[c]	60.7	31.8	25.9[c]	33.8	46.6	56.7	39.2	63.6	30.9	49.0	52.2	C	
A2-8	171.9	33.0	19.7	26.4	60.6	32.8[e]	27.5	33.8[e]	46.7	58.2	35.9	67.9	28.3	49.9	51.5	C	12.2, 14.5, 128.8, 137.6, 167.1
A2-9	170.9	33.0	19.5	26.8	60.6	33.7[e]	27.4	31.9[e]	46.4	58.9	35.8	67.5	27.5	50.4	51.5	C	11.3, 16.7, 26.6, 41.1, 167.2
A2-10	171.3	32.9	19.8	26.3	60.5	33.8[e]	27.6	32.7[e]	46.8	58.9	35.1	67.8	28.3	49.9	51.5	C	14.7, 19.0, 126.4, 139.6, 166.2
A2-11	172.0	32.7	18.9	26.3	60.6	33.8[e]	27.0	32.2[e]	46.7	57.5	37.3	67.3	28.9	50.5	53.1	C	12.4, 60.0, 127.1, 143.2, 166.8
A2-12	171.7	32.9	19.3	27.3	60.8	32.2	26.4	33.9	46.7	57.6	36.4	67.7	29.0	50.2	52.7	C	14.2, 20.7, 35.4, 41.7, 68.4, 124.1, 134.4, 171.5
A2-13	171.3	33.0	19.7	26.5	60.7	34.1[e]	27.5	32.4[e]	46.8	58.2	36.4	68.4	28.7	49.8	51.9	C	56.0, 110.4, 111.8, 123.0, 123.6, 148.6, 152.9, 171.0

Table 2—*Continued*

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-17	S[a]	Substituent signals
A2-14	171.0	33.0	19.7	27.5	60.6	32.4	26.5	34.0	46.7	58.2	36.6	68.3	28.6	49.9	51.8	C	56.0, 110.4, 111.9, 123.0, 123.7, 148.6, 153.0, 165.6
A2-15	171.6	33.1	19.5	26.6	60.7	34.2[e]	27.3	32.6[e]	46.9	57.6	36.1	68.0	28.7	49.9	52.1	M	110.3, 116.1, 122.9, 123.4, 160.9
A2-16	171.9	32.9	19.4	26.2[c]	60.7	31.8	27.4[c]	34.0	46.6	61.8	40.5	67.9	32.8	51.0[d]	52.9[d]	C	
A2-17	172.1	33.0	19.4	27.7	61.8	33.6[e]	22.7	31.7[e]	47.0	71.4	27.7	25.7	20.3	69.6	65.2	C	
A2-19	171.5	73.8	68.4	33.0[c]	58.2	34.3[e]	26.6[c]	32.0[e]	48.3	64.0	31.7	24.5	24.8	55.3	52.6	C	
A2-20	171.5	70.9	70.3	32.5[c]	57.8	34.0[e]	26.3[c]	31.7[e]	48.3	64.1	30.2	24.4	24.3	55.4	52.1	C	15.5, 20.1, 127.8, 139.2, 167.8
A2-21	173.8	68.2	26.3	24.5	61.6	33.9[e]	27.4	32.2[e]	47.8	57.3	39.6	64.3	31.5	49.3	52.3	C	
A2-22	173.8	67.7	26.1[c]	24.3[c]	61.2	35.5[e]	27.2	32.2[e]	47.8[d]	57.8	35.8	67.9	28.3	49.7[d]	51.7	C	15.9, 20.7, 128.1, 137.5, 167.3
A2-23	173.2	68.0	27.3	24.5	61.3	32.4	26.3	33.7	47.9	57.8	35.4	68.0	28.1	49.6	51.3	C	12.1, 14.4, 129.2, 137.1, 167.4
A2-24	171.5	32.9	19.8	27.7	59.5	41.3[e]	73.1	39.3[e]	45.4	56.7	42.0	63.4	32.1	48.5	52.3	C	
A2-25	171.0	32.7	19.7	27.6	59.3	41.0[e]	72.9	39.2[e]	45.1	57.6	38.9	66.5	29.6	49.3	52.1	C	15.8, 20.6, 127.9, 137.7, 167.1
A2-26	172.7	32.8	19.2	26.8	61.1	31.7[e]	27.3	30.8[e]	47.1	60.9	72.8	66.9	27.1	49.4	52.3	W[g]	
A2-27	178.6	34.5	20.7	25.3	65.3	32.5	27.8	32.3	49.1	63.1	70.5	69.8	28.8	52.3	53.4	?	113.1, 119.7, 123.5, 128.2, 163.3
A2-28	173.8	75.6	69.6	27.1	59.3	35.3[e]	31.8	33.4[e]	49.9	58.7	39.9	65.3	34.2	50.3	53.0	W	
A2-29	171.8	74.3	68.0	26.5	57.7	33.4[e]	27.5	32.2[e]	48.3	57.4	34.6	68.4	32.4	49.4	50.5	C	110.3, 116.1, 122.9, 123.4, 160.8
A2-30	174.0	68.0	24.7	27.5	60.5	39.2	72.7	40.9	46.3	57.0	42.0	63.7	32.7	48.6	52.4	C	
A2-31	173.7	67.9	24.6	27.5	60.4	40.9[e]	72.7	39.2[e]	46.3	58.1	38.9	66.6	29.7	49.6	52.4	C	16.0, 20.8, 128.0, 137.7, 167.2
A2-32	171.2	31.8	19.2	103.5	142.2	33.4	24.4	33.0	47.5	63.4	28.2	21.6	22.8	56.6	54.9	C	
A4-1	56.7	49.0	207.3	44.0	57.1	32.6	26.3	36.4	56.7	64.2	35.0	26.4	25.4	55.8	53.3	C	10.4
A4-2	155.6	98.9	192.5	39.3	60.3	31.1	25.8	34.5	57.5	63.6	31.5	24.8	23.7	55.2	51.1	C	
A4-3	155.8	101.9	191.9	39.9	61.6	30.4	24.5	33.5	57.5	70.8	27.8	23.0	20.3	69.8	65.1	C	
A4-4	155.3	99.0	192.3	39.6	60.4	31.5	25.7	34.1	57.5	56.6	37.7	65.0	30.6	48.6	50.6	C	
A4-5	140.2	117.7	178.5	116.0	153.9	32.7	21.1	35.0	57.7	63.1	22.4	25.5	19.0	54.0	52.2	C	
A4-6	147.9	117.7	180.5	116.3	156.9	33.5	21.5	36.4	59.2	57.0	29.8	66.3	26.3	49.0	52.6	M	
A8-1	55.9	25.4	23.6	29.8	66.6	51.8	—[f]	54.3	62.1	66.6	34.9	23.3	25.4	55.1	54.6	C	
A10-1	42.2	25.0	24.6	28.8	59.0	32.4	22.7	43.8	172.1	58.7	22.4	25.4	18.8	53.9	46.6	C	
A10-2	42.7	25.1	24.8	29.1	59.4	32.4	22.6	43.2	172.9	52.0	29.3	65.3	25.1	47.8	46.1	M	
A10-3	42.6	24.8	22.6	26.0	59.2	32.4	22.6	43.1	172.0	52.6	29.1	69.0	25.1	48.3	45.9	M	110.1, 115.7, 122.8, 123.2, 160.5
A10-4	40.2	21.2	22.1	102.4	139.3	35.4	21.7	44.1	171.2	59.0	23.3	25.2	19.2	54.2	53.3	C	
A10-5	72.8	26.9[c]	16.9	103.0	136.8	35.6	21.5	44.5	172.9	58.5	23.2	25.6[c]	19.3	54.3	53.6	C	
A10-6	73.4	25.5[c]	16.9	102.0	138.4	35.7	21.2	44.3	172.0	58.4	22.4	24.9[c]	19.0	54.3	53.6	C	21.2, 169.7
A10-7	72.2	26.5	16.5	104.0	136.5	36.5	28.0	71.4	174.7	64.1	16.3	25.1	18.8	53.6	51.6	C	
A10-8	73.2	24.8	17.0	101.9	137.3	36.8	25.9	77.8	169.6	62.5	16.8	25.2	18.9	53.8	52.1	C	21.1, 21.3, 169.3, 169.5
A10-9	73.3	24.9	16.6	101.7	137.6	36.9	25.1	78.2	169.6	61.6	16.6	25.0	18.9	53.8	52.3	C	21.1, 21.3, 168.8, 169.1
A15-1	56.2	25.8	24.6	29.5	65.8	32.1	27.3	36.5	61.5	58.6	32.1	19.9	32.7	170.6	40.2	C	
A15-2	50.0	26.6	20.6	33.7	55.4	37.6	20.3	37.1	55.3	59.1	33.1	21.4	32.1	169.0	40.5	C	10.8
A17-1	56.9	25.4	24.1	30.3	64.9	44.2	27.3	35.1	63.2	61.4	33.6	25.5	25.5	42.4	169.8	C	
A17-3	50.1	26.1	20.4	36.1	54.3	49.7	20.8	35.6	56.9	61.9	33.6	25.4	25.4	42.3	170.0	C	10.0
A17-4	49.3	25.9	19.9	33.5	57.0	43.7	21.1	35.2	56.2	62.2	30.6	25.4	25.3	42.4	170.6	C	8.2, 11.9
A17-5	49.7	26.3	20.5	33.6	57.3	44.8	21.9	35.6	56.6	62.1	31.7	25.7	25.7	42.5	169.3	C	15.2, 17.4, 22.3
A2, 17-1	171.0	33.2	19.5	32.9	59.0	43.7	27.1	33.9	48.1	61.2	33.5	25.1	25.3	43.1	167.0	C	
A2, 17-2	171.1	32.6	19.2	32.7	58.8	43.6	26.7	33.2	47.9	53.9	29.8	26.0	18.4	72.3	168.9	C	
A13, 17-1	56.6	25.4	24.5	30.2	64.7	43.9	26.5	34.3	62.4	59.2	48.2	—[f]	40.4	41.0	—[f]	C	

Table 2—*Continued*

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-17	S[a]	Substituent signals
B-1	57.2	25.3	24.9	30.0	66.3	35.6	36.8	35.6	55.8	66.3	30.0	24.9	25.3	57.2	55.8	C	
B-4	51.0	25.0	20.5	34.2	56.2	40.8	30.1	35.7	49.4	66.9	31.1	25.1	25.6	57.4	57.3	C	12.3
B-5	57.1	25.1	24.7	29.4	65.2	37.2	44.6	71.6	62.5	67.7	25.3	24.3	25.0	57.2	55.4	C	
B-6	51.8	25.8	20.4	33.9	55.8	40.1	25.4	40.1	49.3	55.8	33.9	20.4	25.8	51.8	49.3	C	12.9, 12.9
B2-1	168.8	33.0	19.9	27.7	58.7	34.5	35.5	34.4	42.2	65.8	30.5	24.9	25.8	58.3[e]	56.8[e]	C	
B2-2	—[f]	33.1	19.8	27.8	58.7	35.2	35.3	34.5	42.3	63.3	40.1	69.6	34.2	55.0	56.1	C	
B17-1	56.3	25.6	24.7	30.4	64.7	44.5	29.5	32.6	57.4	59.5	30.0	25.0	25.8	42.5	—[f]	C	
B10, 17-1	42.3	25.3	24.4	31.3	58.8	41.8	24.4	41.8	—[f]	58.8	31.3	24.4	25.3	42.3	—[f]	C	
C-1	55.2	22.3	25.5	28.8	62.9	34.7	19.8	34.7	55.1	62.9	28.8	25.5	22.3	55.2	55.1	C	
C17-1	54.6	19.6	25.3	23.0	59.2	43.9	20.0	35.1	52.9	61.8	33.3	25.5	25.6	42.8	172.2	C	
D-1	163.4	116.3	138.6	104.5	151.9	35.4	20.6	32.4	51.4	62.9	22.3	25.4	18.9	54.2	52.7	C	
D-2	163.6	116.4	138.5	104.4	151.6	35.2	27.5	32.8	44.8	65.9	29.7	24.3	25.2	56.0	63.3	C	
D-3	163.6	116.7	138.8	104.8	151.4	35.2	27.2	32.7	44.9	63.8	39.2	68.7	34.6	54.1	62.6	C	
E-1	55.2	24.6	24.2	29.8	65.0	34.3[e]	33.0	29.7[e]	59.5	59.4		56.6				C	46.3
E-2	55.4	25.6	24.0	29.8	64.5	40.5[e]	72.6	35.5[e]	60.6	55.4		52.0				C	44.9
E-3	56.0	25.3	25.0	29.8	58.0	41.5[e]	70.4	36.9[e]	53.6	57.1		60.1				C	46.6
E-4	56.5	25.2	24.2	30.0	64.8	38.9[e]	73.5	34.4[e]	59.4	54.1		50.2				C	46.9, 128.6, 130.7, 139.3, 164.4
E-5	55.8	25.6	25.2	30.0	59.5	39.0	74.8	34.6	54.5	57.5		59.9				C	46.7, 128.8, 129.0, 131.0, 139.5, 164.8
E2-1	170.0	33.2	20.2	28.0	60.3	32.8	28.1	31.2	48.1	57.0		41.9				C	37.6, 116.5, 136.1
E2-2	170.4	32.6	19.6	27.5	59.5	32.7	29.1	30.7	50.0	59.2		36.7				C	36.3, 118.8, 133.4, 161.5
E2-3	170.1	—[f]	20.0	27.6	59.7	33.0	28.0	29.8	32.7	55.8		39.9				C	35.6, 117.3, 134.6, 52.8, 156.6
E2-4	—[f]	32.4	19.8	27.5	59.7	32.9	27.9	29.9	47.5	55.7		39.7				C	35.6, 117.2, 134.5, 14.5, 61.5, 157.2
E4-1	153.5	96.3	192.2	39.6	58.0	28.7	31.2	31.8	55.8	58.5		57.6				C	31.0, 53.5, 115.0, 136.6,
E4-2	154.7	100.0	207.9	40.0	60.5	28.1	26.3	34.1	57.0	46.2		51.9				C	36.9, 116.8, 134.9
E4-3	154.7	100.0	192.7	40.0	59.8	28.1	26.3	34.1	57.0	46.0		51.2				C	36.2, 117.0, 135.8
E4-4	143.4	118.2	181.2	116.9	158.3	37.9	21.1	33.0	57.7	46.8		50.5				C	35.5, 117.7, 136.5
E4-5	143.0	117.7	181.0	116.6	157.6	37.9	21.1	33.0	57.7	46.7		50.5				C	34.8, 117.6, 136.4,
E8-1	56.7	25.7	24.7	30.5	66.9	54.3	214.3	53.4	73.6	54.6		56.8				C	45.1, 127.2, 128.0, 128.3, 140.8
E8-2	55.4	24.6	22.6	29.0	65.8	51.1	212.2	46.4	61.6	59.4		53.9				C	44.5
E10-1	42.6	25.5	24.7	30.3	59.8	32.4	29.2	39.8	171.6	47.3		491				C	
F-1	163.6	116.5	138.7	104.9	151.2	35.5	26.2	27.7	49.7	52.9		53.9				C	
F-2	163.6	116.5	138.5	105.1	150.9	35.0	21.1	30.0	47.4	58.0		51.2				C	34.8, 117.6, 135.4
F-3	163.9	116.9	139.0	105.1	151.4	35.6	26.4	27.8	49.8	53.0		54.1				C	
F-4	165.5	116.8	141.3	107.8	153.0	37.5	25.9	30.6	51.4	65.9		66.0				C	
F-5	165.5	116.8	141.4	107.9	153.2	36.7	26.0	29.5	51.5	61.2		61.8				C	61.7, 175.5
F11-1	163.0	118.2	139.0	106.3	148.3	35.9	23.4	32.3	48.3	172.0		50.6				C	
G-1	167.7	32.1	119.2	129.6	70.0	46.8	31.5	28.6	51.4	52.4		61.2				B	32.1, 75.7, 115.8, 135.8
G-2	165.8	32.1	119.5	127.2	71.9	47.7	31.3	28.9	48.6	61.0		56.7				B	35.5, 74.5, 115.4, 137.6

[a] S = solvent (C = $CDCl_3$, M = CD_3OD, W = D_2O, D = DMSO-d_6, P = C_5D_5N, B = C_6D_6, AN = CD_3CN).
[b] According to Ref. 28 the original assignments of C-7 and C-9 have been interchanged.
[c,d] Interchanged to match the expected substituent effect.
[e] By analogy with sparteine and lupanine the assignments of C-7 and C-9 may be interchanged.
[f] Chemical shift not reported.
[g] D_2O + DCl.
[h,i] Interchangeable, as given in the literature. The signals are marked as interchangeable only if the difference is larger than 0.5 ppm.

Table 3. ^{13}C chemical shifts δ (ppm) of the protonated compounds

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-17	S[a]	Substituent signals
Monoprotonated compounds																	
Sparteine derivatives																	
$(A\text{-}1)^+ \cdot ClO_4^-$	55.2	24.3	22.9	28.5	65.2	32.2	25.9	32.2	60.4	61.9	23.1	22.1	17.6	52.1	46.4	D	
$(A\text{-}1)^+ \cdot ClO_4^-$	56.3	25.4	23.9	29.8	66.7	33.5	27.0	33.5	61.8	63.6	24.2	23.2	18.6	53.4	47.9	AN	
$(A\text{-}2)^+ \cdot I^-$	68.5	18.8	23.5	21.9	73.6	34.0	25.1	34.1	69.2	57.3	26.3	25.1	19.3	51.4	44.6	?	44.1
$(A\text{-}4)^+ \cdot ClO_4^-$	60.6	34.7	23.6	30.5	67.2	33.8	27.1	34.0	58.1	64.4	24.2	23.6	18.7	53.5	48.3	AN	20.4
$(A\text{-}6)^+ \cdot ClO_4^-$	71.0	35.7	22.9	30.0	67.2	33.7	27.3	34.0	59.4	65.2	24.6	23.7	18.7	53.7	48.8	AN	128.0, 128.4, 130.0, 144.2
$(A\text{-}15)^+ \cdot ClO_4^-$	55.9	25.2	23.3	28.8	67.3	33.1	27.9	33.5	61.8	64.5	22.3	21.1	25.1	64.8	41.0	AN	129.2, 129.5, 129.5, 139.9
$(A\text{-}16)^+ \cdot I^-$	54.5	24.9	21.6	28.4	65.5	30.5	26.7	32.4	60.4	71.4	26.4	23.6	19.4	68.1	63.8	?	46.8
$(A\text{-}19)^+ \cdot ClO_4^-$	60.3	37.7	21.9	29.7	62.7	33.9	26.5	33.9	54.6	64.5	24.0	22.8	18.7	54.4	48.3	AN	26.2, 119.1
$(A\text{-}20)^+ \cdot ClO_4^-$	70.8	40.0	22.2	29.0	63.3	33.9	26.8	33.9	55.8	65.1	24.2	22.7	18.8	54.9	48.9	AN	126.7, 128.9, 130.5, 139.9, 118.2
$(A\text{-}23)^+ \cdot ClO_4^-$	52.6	18.5	16.5	30.8	187.9	37.5	20.0	31.3	60.6	62.0	25.1	21.2	18.7	53.5	47.1	D	
$(A\text{-}30)^+ \cdot ClO_4^-$	56.4	25.3	23.6	29.0	67.3	33.3	27.4	33.1	61.3	60.9	20.9	22.0	113.2	149.3	47.3	AN	128.0, 128.5, 129.1, 139.8
$(A2\text{-}18)^+ \cdot I^-$	171.2	32.5	19.1	26.4	61.1	29.8	25.9	31.4	46.3	70.8	26.3	21.9	19.4	67.8	62.9	D	45.6
$(A2\text{-}33)^+ \cdot ClO_4$	169.7	32.0	20.0	25.3	58.7	31.3	24.7	36.5	44.1	187.0	31.0	16.3	18.6	53.0	54.0	D	
$(A2\text{-}34)^+ \cdot ClO_4$	169.6	32.3	19.4	27.1	59.2	37.6	21.5	31.9	46.5	66.5	32.5	22.2	26.0	60.6	177.9	D	
$(A4\text{-}2)^+ \cdot ClO_4^-$	156.3	102.0	191.8	39.5	59.1	30.1[b]	23.4	31.8[b]	55.2[c]	61.8	21.8	23.0	17.4	53.5[c]	45.0	D	
$(A4\text{-}4)^+ \cdot ClO_4^-$	157.4	104.7	193.4	40.3	61.2	31.6	24.9[b]	32.8	57.2	58.4	31.3	61.7	25.4[b]	49.1	46.3	AN	
$(A15\text{-}3)^+ \cdot I^-$	53.5	20.0	16.3	31.7	189.4	33.7	19.0	32.7	58.6	54.7	28.9	18.1	32.3	169.4	42.4	D	
$(A17\text{-}2)^+ \cdot I^-$	67.5	21.9	18.7	24.0	70.3	32.9	25.0	40.8	67.9	59.8	31.7	24.2	24.5	41.5	166.3	D	40.7
$(A17\text{-}6)^+ \cdot ClO_4^-$	52.9	19.8	16.1	32.1	183.0	46.2	18.1	30.8	60.0	62.0	31.5	24.4	24.6	43.4	160.8	D	
α-Isospartein derivatives																	
$(B\text{-}1)^+ \cdot ClO_4^-$	55.8	23.8	22.8	28.0	65.8	32.2	32.8	32.2	55.4	65.8	28.0	22.8	23.8	55.8	55.4	D	
$(B\text{-}2)^+ \cdot I^-$	64.0	21.9	19.3	23.4	73.0	33.9	33.6	34.4	68.2	62.3	28.8	24.1	24.9	54.5	51.5	D	43.8
β-Isospartein derivatives																	
$(C\text{-}1)^+ \cdot ClO_4^-$	53.0	18.4	22.5	24.1	62.6	32.8	19.6	32.8	51.8	62.6	24.1	22.5	18.4	53.0	51.8	D	
$(C17\text{-}1)^+ \cdot ClO_4^-$	55.0	17.8	23.3	22.5	59.7	42.9	18.2	33.0	51.7	62.2	32.8	24.9	25.4	45.8	170.3	D?	
Tricyclic compounds																	
$(E4\text{-}1)^+ \cdot ClO_4$	156.2	101.9	191.6	39.6	58.5	26.7	27.6	29.9	54.4	55.9		133.4				D	28.3, 51.4, 57.0
$(E4\text{-}2)^+ \cdot ClO_4^-$	162.7	102.9	199.4	40.6	62.1	28.0	26.2	34.5	58.5	46.5		57.0				W	36.0, 123.2, 134.6
Diprotonated compounds																	
Sparteine derivatives																	
$(A\text{-}1)^{2+} \cdot 2ClO_4^-$	55.2	22.2	22.2	26.4	65.3	28.6	22.2	31.5	56.5	62.3	30.8	21.6	22.2	54.2	48.1	D	
$(A\text{-}3)^{2+} \cdot 2I^-$	62.1	18.7	22.8	20.5	68.9	29.8	22.4	29.8	65.9	68.9	21.1	24.0	17.7	61.2	48.7	W?	71.9
$(A\text{-}7)^{2+} \cdot 2ClO_4^-$	49.5	22.3	16.7	30.6	62.7	34.6	16.7	31.7	52.2	62.7	30.6	21.8	22.3	54.0	48.1	D	14.3
$(A\text{-}23)^{2+} \cdot 2ClO_4^-$	53.5	19.7	16.1	31.6	186.9	35.3	16.5	30.8	58.6	61.4	22.1	21.6	17.4	52.8	45.2	D	
$(A\text{-}25)^{2+} \cdot 2ClO_4^-$	197.6	37.0	16.5	26.2	65.9	31.3	23.6	34.1	55.5	65.2	31.8	22.3	23.6	59.1	56.7	AN	26.2
$(A\text{-}26)^{2+} \cdot 2ClO_4^-$	194.3	37.9	16.7	26.1	65.5	31.4	23.5	34.1	55.9	65.5	31.6	22.6	23.5	59.3	51.4	AN	126.7, 130.4, 132.7, 134.6
$(A\text{-}26)^{2+} \cdot 2Cl^-$	199.4	37.4	19.1	28.9	61.6	24.1	22.9	30.5	48.9	57.4	30.5	23.0	22.5	53.5	44.9	D	127.8, 129.7, 133.0, 136.6
$(A\text{-}26)^{2+} \cdot 2Br^-$	208.6	34.8	20.2	30.5	64.1	27.9	24.0	32.1	51.1	59.8	32.2	23.1	23.4	53.9	48.4	W	129.2, 133.0, 134.4, 146.2
$(A\text{-}27)^{2+} \cdot 2Cl^-$	204.3	—[e]	20.0	30.0	64.3	27.1	23.5	31.3	49.4	59.2	32.1	22.8	23.2	56.0	48.3	W	
$(A\text{-}30)^{2+} \cdot 2Cl^-$	56.8	23.4	22.5	28.2	67.1	30.8	28.0	32.3	57.8	64.2	30.0	19.9	33.5	192.6	40.0	W	128.4, 129.9, 135.1, 137.1
$(A\text{-}31)^{2+} \cdot 2ClO_4^-$	52.9	19.7	15.9	31.7	186.2	33.7	17.0	33.7	55.3	186.2	31.7	15.9	19.7	52.9	55.3	D	
α-Isosparteine derivatives																	
$(B\text{-}1)^{2+} \cdot 2ClO_4^-$	56.5	23.2	22.1	27.0	65.3	31.4	29.2	31.4	51.3	65.3	27.0	22.1	23.2	56.5	51.3	D	
$(B\text{-}3)^{2+} \cdot 2I^-$	62.0	20.7	18.3	22.9	68.6	30.1	31.1	30.1	59.1	68.6	22.9	18.3	20.7	62.0	59.7	D	64.2
β-Isosparteine																	
$(C\text{-}1)^{2+} \cdot 2ClO_4^-$	53.5	16.5	23.1	23.4	61.8	33.0	18.6	30.5	49.4	63.3	32.1	22.5	23.1	55.5	54.8	D	

[a] S = solvent (C = $CDCl_3$ M = CD_3OD, W = D_2O, D = DMSO-d_6, P = C_5D_5N, B = C_6D_6, AN = CD_3CN).
[b,c,d] Marked as interchangeable in the literature.
[e] Chemical shift not reported.

Table 4. Substituent effects (ppm) in the free bases, in $CDCl_3$

Compound	α	β	γ	δ
Sparteine derivatives				
2α-OH (e)[a]	32.6	$5.7_{CH_2\text{-}3}$	$1.7_{C=O\text{-}10}$, $-2.5_{C\text{-}6}$, $-4.9_{CH_2\text{-}4}$	$0.6_{CH\text{-}5}$, $0.2_{CH\text{-}7}$, $0.4_{CH\text{-}9}$
2α-OAc (e)[a]	32.2	$4.3_{CH_2\text{-}3}$	$0.8_{C=O\text{-}10}$, $-0.9_{C\text{-}6}$, $-5.2_{CH_2\text{-}4}$	$-0.4_{CH\text{-}5}$, $0.3_{CH\text{-}7}$, $0.2_{CH\text{-}9}$
2α-Me (e)	2.0	$9.7_{CH_2\text{-}3}$	$-0.1_{CH\text{-}6}$, $0.0_{CH_2\text{-}4}$, $-4.5_{CH_2\text{-}10}$	$0.9_{CH\text{-}7}$, $1.1_{CH_2\text{-}5}$, $0.4_{CH\text{-}9}$
2α-Ph (e)	13.3	$11.4_{CH_2\text{-}3}$	$0.6_{CH\text{-}6}$, $0.1_{CH_2\text{-}4}$, $-3.2_{CH_2\text{-}10}$	$0.9_{CH\text{-}7}$, $0.9_{CH_2\text{-}5}$, $0.3_{CH\text{-}9}$
2β-CN	-0.7	$-5.3_{CH_2\text{-}3}$	$-5.9_{CH\text{-}6}$, $1.2_{CH_2\text{-}4}$, $-2.6_{CH_2\text{-}10}$.	$-0.4_{CH\text{-}7}$, $-0.3_{CH\text{-}9}$, $-0.6_{CH_2\text{-}5}$
3β-OH (e)[b]	34.8	$2.2_{C=O}$, $6.5_{CH_2\text{-}4}$	$-2.4_{CH_2\text{-}5}$	$0.5_{CH\text{-}6}$, $0.9_{CH_2\text{-}10}$
8-*anti*-OH (e)	46.5	$7.5_{CH\text{-}7}$, $7.3_{CH\text{-}9}$	$-1.7_{CH\text{-}6}$, $-0.6_{CH\text{-}11}$, $-1.5_{CH_2\text{-}10}$, $-0.5_{CH_2\text{-}17}$	$0.7_{CH_2\text{-}5}$, $1.5_{CH_2\text{-}12}$
9β-OH (e)	33.1	$4.1_{CH\text{-}11}$, $-9.1_{CH_2\text{-}8}$, $7.0_{CH_2\text{-}10}$	$0.8_{CH\text{-}7}$, $-8.2_{CH_2\text{-}12}$	$-0.9_{CH\text{-}6}$, $0.0_{CH_2\text{-}2}$, $0.3_{CH_2\text{-}13}$, $-0.3_{CH_2\text{-}17}$
12α-OH (e)[b]	37.1	$2.5_{CH\text{-}11}$, $6.4_{CH_2\text{-}13}$	$-2.8_{CH_2\text{-}9}$, $-5.4_{CH_2\text{-}14}$	$-0.6_{CH_2\text{-}15}$, $-0.4_{CH_2\text{-}17}$, $0.4_{CH_2\text{-}8}$, $0.2_{CH_2\text{-}10}$
13β-OH (e)[b]	43.4	$7.0_{CH_2\text{-}12}$, $7.6_{CH_2\text{-}14}$	$-2.4_{CH\text{-}11}$, $-4.6_{CH_2\text{-}15}$	$-0.9_{CH\text{-}9}$
15β-Ph (e)	13.7	$10.0_{CH\text{-}14}$	$-0.2_{CH\text{-}11}$, $0.2_{CH_2\text{-}13}$, $-3.5_{CH_2\text{-}17}$	$0.5_{CH\text{-}7}$, $0.9_{CH\text{-}9}$, $-0.5_{CH_2\text{-}12}$
17β-Me (e)	3.4	$10.3_{CH\text{-}7}$	$0.5_{CH\text{-}11}$, $0.2_{CH\text{-}6}$, $-0.1_{CH_2\text{-}8}$, $-3.2_{CH_2\text{-}15}$	$1.0_{CH\text{-}9}$, $0.3_{CH_2\text{-}5}$, $0.8_{CH_2\text{-}12}$, $0.5_{CH_2\text{-}14}$,
17β-Et (e)	7.1	$7.0_{CH\text{-}7}$	$0.3_{CH\text{-}6}$, $-0.2_{CH\text{-}11}$, $0.3_{CH_2\text{-}8}$, $-3.5_{CH_2\text{-}15}$	$1.0_{CH\text{-}9}$, $0.3_{CH_2\text{-}5}$, $1.0_{CH_2\text{-}12}$, $0.7_{CH_2\text{-}14}$
6β-Me (a)	-10.9	$5.6_{CH\text{-}7}$, $4.1_{CH_2\text{-}5}$	$-6.4_{CH_2\text{-}2}$, $-4.2_{CH_2\text{-}4}$, $-6.8_{CH_2\text{-}8}$, $-6.1_{CH_2\text{-}10}$, $0.7_{CH_2\text{-}17}$	$0.3_{CH\text{-}9}$, $0.6_{CH_2\text{-}3}$
6β-Et (a)	-9.0	$3.2_{CH\text{-}7}$, $1.1_{CH_2\text{-}5}$	$-7.2_{CH_2\text{-}2}$, $-4.4_{CH_2\text{-}4}$, $-7.3_{CH_2\text{-}8}$, $-6.1_{CH_2\text{-}10}$, $0.6_{CH\text{-}17}$	$-4.2_{CH\text{-}9}$, $1.9_{CH_2\text{-}3}$
6β-OH (a)[b]	24.5	$5.1_{CH\text{-}7}$, $5.4_{CH_2\text{-}5}$	$0.6_{C=O\text{-}2}$, $-0.5_{CH_2\text{-}4}$, $-11.6_{CH_2\text{-}8}$, $-4.3_{CH_2\text{-}10}$, $1.2_{CH_2\text{-}17}$	$0.1_{CH_2\text{-}3}$, $-0.6_{CH\text{-}9}$
13α-OH (a)	40.1	$7.2_{CH_2\text{-}12}$, $7.0_{CH_2\text{-}14}$	$-7.0_{CH\text{-}11}$, $-6.0_{CH_2\text{-}15}$	$-0.3_{CH\text{-}9}$
13α-OAc (a)	44.3	$3.9_{CH_2\text{-}12}$, $3.7_{CH_2\text{-}14}$	$-5.9_{CH\text{-}11}$, $-5.4_{CH_2\text{-}15}$	$-0.2_{CH\text{-}9}$
13α-OTig[b] (a)	43.2	$2.4_{CH_2\text{-}12}$, $3.1_{CH_2\text{-}14}$	$-6.0_{CH\text{-}11}$, $-5.7_{CH_2\text{-}15}$	$-1.1_{CH\text{-}9}$
α-Isosparteine derivatives				
6β-Me (a)	-10.1	$5.2_{CH\text{-}7}$, $4.2_{CH_2\text{-}5}$	$-6.8_{CH_2\text{-}2}$, $-4.4_{CH_2\text{-}4}$, $-6.5_{CH_2\text{-}8}$, $-6.4_{CH_2\text{-}10}$, $1.5_{CH_2\text{-}17}$	$0.1_{CH\text{-}9}$, $-0.3_{CH_2\text{-}3}$
9β-OH (e)	36.0	$1.4_{CH\text{-}11}$, $7.8_{CH_2\text{-}8}$, $6.7_{CH_2\text{-}10}$	$1.6_{CH\text{-}7}$, $-4.7_{CH_2\text{-}12}$	$-1.1_{CH\text{-}6}$, $-0.1_{CH_2\text{-}2}$, $-0.6_{CH_2\text{-}13}$, $-0.0_{CH_2\text{-}15}$, $-0.4_{CH_2\text{-}17}$
11β-Me (a)[c]	-11.1	$4.4_{CH\text{-}9}$, $2.8_{CH_2\text{-}12}$	$-4.7_{CH_2\text{-}8}$, $-0.1_{CH_2\text{-}10}$, $-4.7_{CH_2\text{-}13}$, $-8.0_{CH_2\text{-}17}$, $-5.6_{CH_2\text{-}15}$	$-0.7_{CH\text{-}7}$, $0.2_{CH_2\text{-}14}$
13β-OH (e)[d]	44.7	$9.6_{CH_2\text{-}12}$, $8.4_{CH_2\text{-}14}$	$-2.5_{CH\text{-}11}$, $-3.3_{CH_2\text{-}15}$	$0.1_{CH\text{-}9}$
Thermopsine				
13β-OH (e)	44.4	$9.5_{CH_2\text{-}12}$, $9.4_{CH_2\text{-}14}$	$-2.1_{CH\text{-}11}$, $-1.9_{CH_2\text{-}15}$	$-0.1_{CH\text{-}9}$
Tricyclic Compounds				
8-*anti*-OH (e)[e]	39.6	$6.2_{CH\text{-}7}$, $5.8_{CH\text{-}9}$	$-0.5_{CH\text{-}6}$, $-4.0_{CH\text{-}11}$, $1.1_{CH_2\text{-}10}$, $-4.6_{CH_2\text{-}13}$	$0.0_{CH_2\text{-}5}$
8-*syn*-OH (a)[e]	37.4	$7.2_{CH\text{-}7}$, $7.2_{CH\text{-}9}$	$-7.0_{CH\text{-}6}$, $-2.3_{CH\text{-}11}$, $-5.9_{CH_2\text{-}10}$, $3.5_{CH_2\text{-}13}$	$0.0_{CH_2\text{-}5}$

[a] Calculated from 10-oxo-5,6-dehydrosparteine derivatives.
[b] Calculated from lupanine and derivatives.
[c] Calculated from 6β, 11β-dimethyl-α-isosparteine.
[d] Calculated from isolupanine.
[e] Calculated from tricyclic *N*(12)-methyl derivatives (E-2 and E-3).

Table 5. Effects of oxo groups (ppm), in $CDCl_3$

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-17
Sparteine derivatives															
2-Oxo	115.4	7.5	−4.8	−2.3	−5.3	−0.5	0.1	−1.0	−15.0	0.0	−1.0	0.0	−0.6	0.4	−0.5
8-Oxo	−0.1	−0.2	−0.9	0.7	0.3	18.9	—	18.4	0.3	2.4	0.4	−1.2	−0.4	−0.1	1.2
10-Oxo	−13.8	−0.6	0.1	−0.3	−7.3	−0.5	−4.7	7.9	110.3	−5.5	−12.1	0.9	−7.0	−1.3	−6.8
15-Oxo	0.2	0.2	0.1	0.4	−0.5	−0.8	−0.1	0.6	−0.3	−5.6	−2.4	−4.6	6.9	115.4	−13.2
17-Oxo	0.9	−0.2	−0.4	1.2	−1.4	11.3	−0.1	−0.8	1.4	−2.8	−0.9	1.0	−0.3	−12.8	116.4
α-Isosparteine derivatives															
2-Oxo	168.8	7.7	−5.0	−2.3	−7.6	−1.1	−1.3	−1.2	−13.6	−0.5	0.5	0.0	0.5	1.1	1.0
17-Oxo	−0.9	0.3	−0.2	0.4	−1.6	8.9	−7.3	−3.0	1.6	−6.8	0.0	0.1	0.5	−14.7	—
β-Isosparteine															
17-Oxo	−0.6	−2.7	−0.2	−5.8	−3.7	9.2	0.2	0.4	−2.2	−1.1	4.5	0.0	2.8	−12.4	117.1

counterparts; the magnitude of the downfield shifts depends on the degree of substitution. As expected, the γ-effects reflect the steric interactions, and greater shielding is experienced by carbons in an eclipsed or *gauche* position to the substituent. Obviously, the variation of the γ-substituent effects results from different degrees of skeletal twisting caused by the substituent or from the conformational equilibrium. That is why in the case of quinolizidine alkaloids and especially of tri- and tetracyclic representatives the substituent effects can be used to speculate on the position of the substituent and configuration of the substituted carbon atom, but no general rules could be drawn only on the base of the existing empirical data. However, having the possible conformational situation in mind, one can assign the ^{13}C signals in many cases on the basis of the supposed substituent effects. After comparison with unsubstituted or related compounds, many of the assignments published in the literature have been interchanged by us (A-5, A-10, A-12, A2-4, A2-7, A2-16, A2-19, A2-20, A2-22, A10-5, A10-6 and B2-1).

As expected 2-, 8- and 15-oxo groups influence mainly their neighbouring atoms. The effects of the 2-oxo groups are similar for sparteine and α-isosparteine and almost symmetrical with respect to 15-oxosparteine. It is known that an oxo group at C-10 changes the geometry of the compound. The conformational conversion of the rings C and D from *trans*-boat–chair in sparteine to *cis*-chair–chair in aphylline is associated with strong shielding effects on C-8, C-12, C-14 and C-17.[13] On the basis of ^1H NMR data it is proposed that the geometry of 17-oxosparteine with ring C in sofa conformation differs from that of the parent compound sparteine.[21] There are no published data about the stereochemistry of 17-oxo-α- and -β-isosparteine. The increased shielding of C-9 and C-11 in 17-oxo-α-isoparteine is an indication of a flattering of ring C which places these two atoms in an eclipsed position. A conformational change accompanied by nitrogen inversion towards the all-chair conformation may be the reason for the relatively large effects of the 17-oxo group on C-3, C-5, C-6, C-10, C-12 and C-14 in 17-oxo-β-isosparteine.

Substituent chemical shifts

According to LaLonde and Donvito,[72] the signal of the equatorially situated methyl substituent in 4-methylquinolizidine is at $\delta = 20.8$ while the shift of the axial methyl carbon in 10-methylquinolizidine is only $\delta = 10.1$. Our data are in accordance with the data for quinolizidines (Table 2) with the following sequence of the chemical shifts of the methyl substituents: $\delta < 15$ in an axial position and > 20 in equatorial position.

INFLUENCE OF MOLECULAR GEOMETRY ON ^{13}C CHEMICAL SHIFTS

One of the problems to be solved by the interpretation of ^{13}C NMR spectra of the quinolizidine alkaloids is the determination of the ring conformations. In contrast to the molecules containing six-membered rings with clearly defined geometry, the stereochemical effects on the ^{13}C chemical shifts of quinolizidine alkaloids are not always straightforward to interpret. There are two reasons for this: the possible dynamic conformational

Table 6. Effects of the different stereochemistry of the skeleton on the ^{13}C chemical shifts[a] (ppm), in $CDCl_3$

Compounds	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-17
Sparteine–α-isosparteine	−1.2	0.3	−0.4	−0.9	0.0	−2.7	−9.4	0.3	6.0	−2.1	4.5	−0.4	0.5	−2.0	−2.4
Sparteine–β-isosparteine	0.8	3.3	−1.0	0.3	3.4	−1.8	7.6	1.2	6.7	1.3	5.7	−1.0	3.5	0.0	−1.7
α-Isosparteine–β-isosparteine	2.0	3.0	−0.6	1.2	3.4	0.9	17.0	0.9	0.7	3.4	1.2	−0.6	3.0	2.0	0.7

[a] Calculated as the difference in the chemical shifts of each pair of compounds.

equilibrium and nitrogen inversion and the distortion of the optimum geometry of the six-membered rings caused by substituents. Nevertheless, with the help of ^{13}C chemical shifts useful information about the conformations of the rings can be gained. Table 6 illustrates the differences in the ^{13}C chemical shifts of the three stereoisomeric sparteines.

A very important diagnostic value for the conformation of the rings B and C is the ^{13}C chemical shift of the bridge carbon C-8. A marked shielding appears in sparteine and in β-isosparteine compared with α-isosparteine. This shielding is presumably the result of a close approach of C-8 to the lone pair at N-1 in sparteine having ring C in boat conformation, or the two N-1 and N-16 in β-isosparteine with both rings B and C in boat conformations. The δ-value of C-8 for the tricyclic compound E-1 (see Table 2) reflects the possibility of a dynamic conformational interconversion of ring C between boat and chair. However, in a number of compounds, the position of the C-8 signal may be further changed owing to specific substituent effects and cannot be regarded as a universal probe for the elucidation of the actual conformation of the sparteine skeleton.

In addition to the chemical shift of C-8, some other signals can be indicative of the geometry of the compounds according to their sterical interactions. The change of the conformation of rings C/D from *trans*-boat–chair in sparteine to *cis*-chair–chair in aphylline is connected with a shielding of C-12, C-14 and C-17 and that to *trans*-chair–chair in α-isoparteine with a shielding of C-10 and C-12. The change of the conformation of A/B from chair–chair in sparteine to boat–chair in β-isosparteine is connected mainly with a shielding of C-3, C-6, C-10 and C-12.

The introduction of an equatorial substituent at positions 2, 15 and 17 does not cause any changes relative to the conformation of the parent sparteine.[7] The same is valid for axial alkyl substituents at C-6.[32]

It has been shown[73] that the overall ^{13}C chemical shielding expressed as the sum of all ^{13}C chemical shifts ($\Sigma\delta$) can be diagnostic for differentiating diastereomers, especially when the individual steric effects are not easily visualized or the signals are ambiguously assigned. The smaller value of $\Sigma\delta$ is connected with the more sterically hindered isomer. The values of $\Sigma\delta$ of some diastereomeric compounds given below reveal a reasonable correlation between the sterical hindrance and the overall shielding ($\Sigma\delta$). The values decrease with increase in the number of the unfavoured steric interactions in the respective isomer:

$\Sigma\delta$ = 627.0 (α-isosparteine) > 617.1 (sparteine) > 588.8 (βisosparteine);

$\Sigma\delta$ = 606.3 6β-methyl-α-isosparteine) > 595.6 (6β-methylsparteine);

$\Sigma\delta$ = 672.3 (9β-hydroxy-α-isosparteine) > 661.7 (9β-hydroxysparteine).

PROTONATION EFFECTS

The investigation of the protonation effects of quinolizidine alkaloids is important because of the use of some of their representatives in catalytic reactions with organometallic reagents (see Introduction). The mono- and disalts of tri- and tetracyclic compounds have been extensively studied by Skolik and co-workers,[8–10,12,33,37,39,58,60] and protonation effects in the ^{13}C NMR spectra have been described in detail. The protonation effects expressed as the difference between the chemical shifts of the mono- or disalts and the free base are given in Table 7.

In the monosalts of sparteine a change to the all-chair conformation stabilized by an intramolecular hydrogen bond N^+-1-H$\cdots N^+$-16 takes place. Most indicative for the all-chair skeleton in monosalts of sparteine is the shielding observed on C-2, C-14 and C-17 which are subjected to γ-*gauche* interactions in the *cis*-quinolizidine fragment C/D. The conformation of the disalts of sparteine derivatives is the same as the conformation of the free base, and the changes of the chemical shifts are due only to protonation. The protonation effects are propagated symmetrically with respect to the two nitrogen atoms.

Obviously, the conformational equilibrium is sensitive to a change of solvents, e.g. see the protonation effects for $(A\text{-}1)^+ \cdot ClO_4^-$ in different solvents (Table 7). Protonation effects are also sensitive to the type of the counter-anion, e.g. see the effects for $(A\text{-}26)^{2+}$ in Table 7.

For α-isosparteine there are no conformational effects upon protonation. The differences in the chemical shifts in comparison with those of the free bases are due only to protonation and minor deformations of the protonated four-ring skeleton, caused by the strong intramolecular hydrogen bond between N-1 and N-16. There are only eight signals in the spectra of the mono- and diperchlorates of α-isosparteine, indicating that the structures of the salts are symmetrical, similar to the structure of the free base.

The conformations of the four rings in β-isosparteine differ in all three forms: the free bases and mono- and disalts. In β-isosparteine monoperchlorate the C-3 and C-14, C-4 and C-13, C-5 and C-12, C-10 and C-17 signals are shielded because of γ-effects. The protonation effects on β-isosparteine diperchlorate are different for both quinolizidine parts, proving that the structure is unsymmetrical and differs from that of the uncharged compound.

The substituent effects in protonated compounds are very similar to those of the parent (see Ref. 7). Obviously, the geometry is not changed by substitution.

EXPERIMENTAL

NMR spectra were recorded at a Bruker DRX-250 spectrometer. Standard Bruker software was used for the 1D NOEMULT and 2D experiments. The delay for

Table 7. Protonation effects[a]

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-17	S[b]
Monoprotonated compounds																
Sparteine derivatives																
$(A\text{-}1)^+ \cdot ClO_4^-$	−0.8	−1.3	−1.6	−0.6	−1.1	−0.7	−1.5	−3.7	−1.4	−2.3	−11.4	−2.4	−8.2	−3.1	−7.0	D/C
$(A\text{-}1)^+ \cdot ClO_4^-$	0.3	−0.2	−0.6	0.7	0.4	0.6	−0.4	−2.4	0.0	−0.6	−10.3	−1.4	−7.2	−1.8	−5.5	AN/C
$(A\text{-}4)^+ \cdot ClO_4^-$	2.6	−0.6	−0.9	0.3	1.0	0.0	−0.4	−2.4	0.8	0.0	−10.5	−1.3	−7.3	−1.8	−5.2	AN/C
$(A\text{-}6)^+ \cdot ClO_4^-$	1.7	−1.3	−1.7	0.0	0.3	−0.1	0.3	−2.2	0.8	0.7	−9.9	−1.2	−7.1	−2.0	−5.4	AN/C
$(A\text{-}15)^+ \cdot ClO_4^-$	−0.4	−0.6	−1.8	−0.5	0.7	−0.3	0.2	−3.3	0.1	0.5	−11.7	−3.6	−10.7	−4.1	−8.9	AN/C
$(A\text{-}19)^+ \cdot ClO_4^-$	2.1	−0.6	0.8	−0.2	1.1	0.8	−0.1	−1.9	0.9	0.0	−10.2	−1.9	−6.9	−0.9	−4.9	AN/C
$(A\text{-}20)^+ \cdot ClO_4^-$	2.0	−1.6	0.5	0.0	1.3	−0.9	−0.3	−2.0	0.9	0.7	−9.5	−2.3	−7.0	−1.0	−4.8	AN/C
α-Isosparteine																
$(B\text{-}1)^+ \cdot ClO_4^-$	−1.4	−1.5	−2.1	−2.0	−0.5	−3.4	−4.0	−3.4	−0.4	−0.5	−2.0	−2.1	−1.5	−1.4	−0.4	D/C
β-Isosparteine derivatives																
$(C\text{-}1)^+ \cdot ClO_4^-$	−2.2	−3.9	−3.0	−4.7	−0.3	−1.9	−0.2	−1.9	−3.3	−0.3	−4.7	−3.0	−3.9	−2.2	−3.3	D/C
$(C17\text{-}1)^+ \cdot ClO_4^-$	0.4	−1.8	−2.0	−0.5	0.5	−1.0	−1.8	−2.1	−1.2	0.4	−0.5	−0.6	−0.2	3.0	−1.9	D/C
Diprotonated compounds																
Sparteine derivatives																
$(A\text{-}1)^{2+} \cdot 2ClO_4^-$	−0.8	−3.4	−2.3	−2.7	−1.0	−4.3	−5.2	−4.4	−5.3	−1.9	−3.7	−3.0	−3.4	−1.0	−5.3	D/C
$(A\text{-}3)^{2+} \cdot 2I^-$	6.1	−6.9	−1.7	−8.6	2.6	−3.1	−5.0	−6.1	4.1	4.7	−13.4	−0.5	−8.1	6.0	−4.7	D/C
$(A\text{-}7)^{2+} \cdot 2ClO_4^-$	−0.2	−3.9	−3.6	−2.6	7.3	−3.9	−3.9	−4.5	−3.5	−2.5	−3.8	−3.0	−3.6	−1.5	−6.0	D/C
$(A\text{-}25)^{2+} \cdot 2ClO_4$	55.4	−60.2	−5.8	−0.9	4.9	−1.5	−3.6	−1.9	2.7	1.0	−2.7	−2.6	−2.2	3.7	3.4	AN/C
$(A\text{-}26)^{2+} \cdot 2ClO_4^-$	56.2	−68.0	−3.0	3.0	2.3	−6.0	−4.3	−4.9	−5.3	−5.3	−2.2	−2.2	−2.9	0.5	−4.7	W/C
$(A\text{-}26)^{2+} \cdot 2Cl^-$	55.8	−68.0	−2.9	3.1	2.1	−6.0	−4.3	−3.1	−5.3	−5.2	−2.1	−2.0	−2.8	0.4	−4.7	W/C
$(A\text{-}26)^{2+} \cdot 2Br^-$	59.3	−67.4	−2.6	3.6	1.8	−5.1	−3.8	−4.1	−3.7	−4.5	−2.1	−1.9	−2.5	−1.8	−4.5	W/C
$(A\text{-}27)^{2+} \cdot 2Cl^-$	55.4	−67.1	−2.9	3.0	1.9	−6.1	−4.3	−5.1	−5.4	−5.1	−1.9	−2.3	−2.8	0.3	−4.6	W/C
$(A\text{-}30)^{2+} \cdot 2Cl^-$	−0.5	−2.0	−2.7	−1.4	0.7	−4.2	1.7	−3.4	−5.1	4.0	−0.4	−3.9	−73.9	43.5	−6.9	W/C
α-Isosparteine derivatives																
$(B\text{-}1)^{2+} \cdot 2ClO_4^-$	−1.7	−2.1	−2.8	−3.0	−1.0	−4.2	−7.6	−4.2	−4.5	−1.0	−3.0	−2.8	−2.1	−0.7	−4.5	D/C
β-Isosparteine																
$(C\text{-}1)^{2+} \cdot 2ClO_4$	−1.7	−5.8	−2.4	−5.4	−1.1	−1.7	−1.2	−4.2	−5.7	0.4	3.3	−3.0	0.8	0.3	−0.3	D/C

[a] Calculated as difference in the chemical shifts of the protonated compounds and the corresponding free bases.
[b] Solvent of the protonated compound/solvent of the free base (see Table 3 for solvent code).

inversion–recovery in HMQC spectra was 0.6 s for thermopsine and 0.5 s for anagyrine.

All ^{13}C chemical shifts were compiled in a database using MDL ISIS-Base.

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