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The Chemistry of Castanospermine, Part I: Synthetic Modifications at C-6

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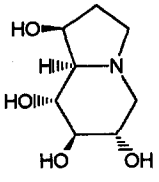
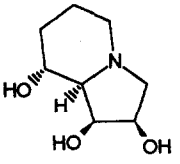
Abstract: *Methodology for the selective functionalisation of castanospermine is outlined which has allowed the synthesis of a number of analogues selectively modified at C-6. Australine and some australine analogues have also been synthesized from castanospermine.*

INTRODUCTION

Castanospermine (1(S), 6(S), 7(R), 8(R), 8a(R)-tetrahydroxyoctahydroindolizidine) (1), which occurs in the seeds of the Australian legume *Castanospermum australe*[1] and the pods of *Alexa leiopetala*[2], is one of a number of plant derived polyhydroxy alkaloid glycosidase inhibitors such as swainsonine (2), deoxynojirimycin (3) and DMDP (4) that have wide ranging biological effects[3]. Castanospermine is a potent inhibitor of several glucosidases[4-7] including mammalian intestinal sucrase[8] and the glucosidase involved in lysosomal glycoprotein processing[9-11], and castanospermine and some of its derivatives may have potential utility in the treatment of viral infections[12-21], cancers[22-29], malaria[30], and diabetes[23,31-33]. Not surprisingly, there has been considerable interest in the synthesis of castanospermine as well as a number of its stereoisomers and analogues[34].



(1)



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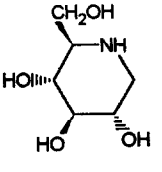

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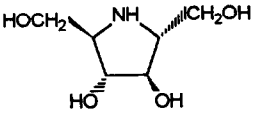


(4)

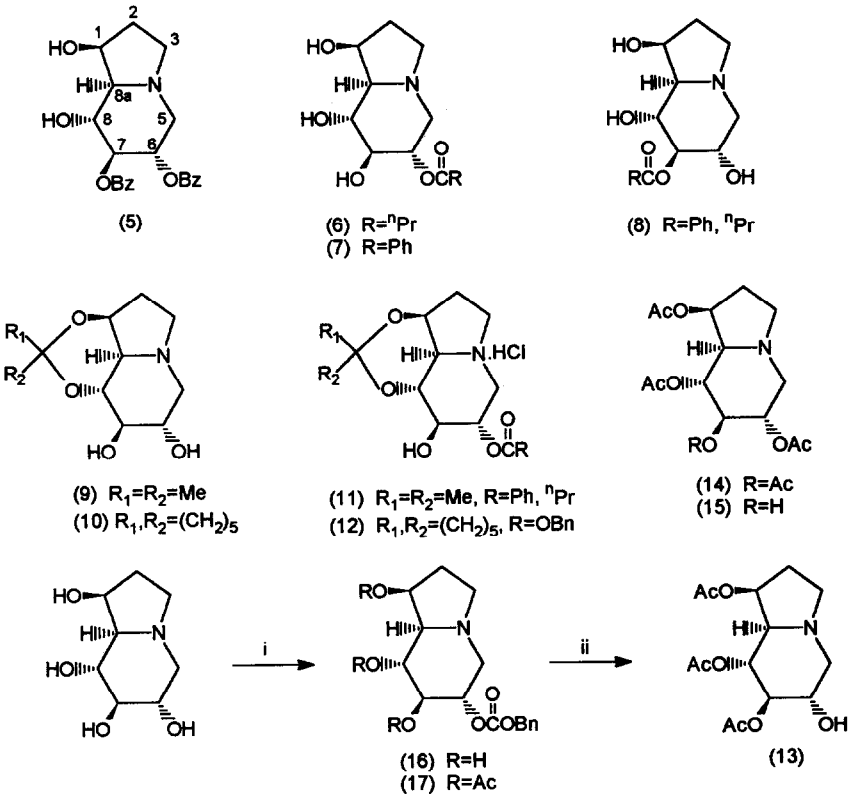
A few years ago we initiated a systematic study of the biological activity of structurally modified castanospermine compounds. As the published total syntheses of castanospermine do not readily provide sufficient quantitities of material we turned to isolation of the natural product as a source for starting material. The published procedure,[31,32] with minor modifications, proved adequate and a 1 kg supply of crystalline castanospermine was readily obtained. This paper describes some of the chemistry we have pursued on the selective modification of castanospermine at the C-6 position. Future publications will outline our efforts on selectively modifying other parts of the molecule while the biological results will be reported elsewhere.

In order to selectively modify castanospermine at C-6 it is necessary to protect the other three hydroxy groups and/or selectively protect the 6-hydroxy group. When this work was begun there were no published reports on selective protection of castanospermine's hydroxy groups. Recently however, several protection strategies have been published. The Merrell Dow group have described the preparation of separable mixtures of 6-*O*- and 7-*O*- monoesters in very poor yield (<10%) and also the 6,7-dibenzoate (5) in 48% yield by direct acylation of castanospermine with pyridine and acyl halides[29,33,35]. This dibenzoate was subsequently utilised for the synthesis of the 6-butyrate (6) and 6-benzoate (7) as well as the corresponding 7-monoesters (8)[36] all of which were prepared as potential anti-AIDS agents. The syntheses preceeded *via* diols (9) or (10) which were available from dibenzoate (5) by acetal formation followed by saponification. Conventional acylation (RCOCl, THF or CH_2Cl_2) of diol (9) gave selectively the 6-ester hydrochlorides (11) from which the monoesters (6) and (7) were obtained after hydrolysis. Alternatively, the 6-carbonate (12) was readily prepared from diol (10), and after acylation of the remaining hydroxy group, hydrogenolysis and then hydrolysis, the 7-esters (8) were obtained. An enzyme catalysed regioselective acylation of castanospermine has been reported whereby a number of 1-*O*-acyl derivatives were prepared using the protease subtilisin as catalyst. Further acylation of these derivatives catalysed by a lipase provided 1,7-di-*O*-acyl derivatives which could be selectively hydrolysed by subtilisin to give 7-*O*-monoesters[37]. In another approach castanospermine was treated with dibutyltin oxide in methanol followed by the addition of triethylamine and an acyl halide. A number of 6-*O*-monoesters were prepared in this way in moderate yield (≤40%)[38].

RESULTS AND DISCUSSION

We have devised two routes to 1,7,8-tri-*O*-acetylcastanospermine (13), from which we anticipated being able to synthesize some castanospermine analogues. Selective deprotection of castanospermine tetraacetate (14) with tributyltin methoxide afforded a moderate yield of the 6- and 7-hydroxy compounds (13) and (15) in a 1.75:1 ratio along with some starting material and traces of dihydroxy compounds. While this provided quick access to the desired triacetate (13), separation of the isomers (13) and (15) was tedious on a large scale so an alternative procedure was developed.

The use of organotin derivatives to facilitate the regioselective manipulation of polyols is well established[39], and this methodology was applied to castanospermine. After treating castanospermine separately with dibutyltin oxide and bis(tributyltin) oxide, the resulting stannyl derivatives were examined for efficacy of regioselective acylation. The compound obtained on treating castanospermine with 2.5 equiv. of bis(tributyltin) oxide in refluxing toluene proved the most useful as 6-*O*-monoesters were the sole products on further treatment with acyl halides, and excellent yields of crystalline monoesters (6)

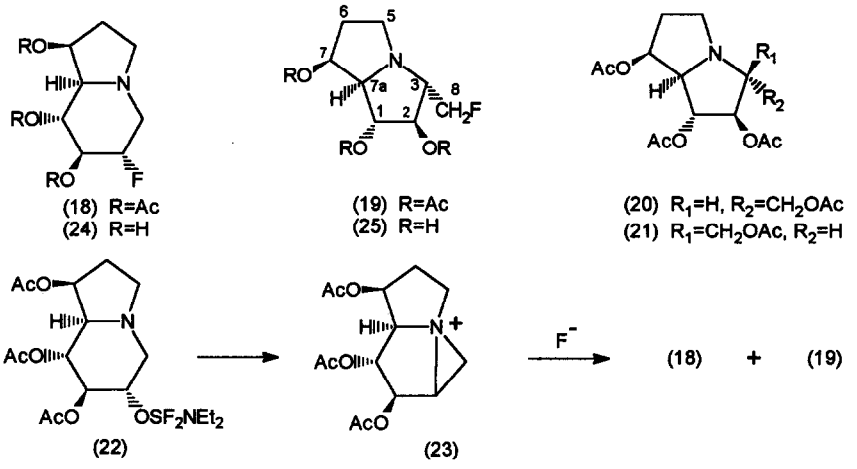


Reagents: i) $(Bu_3Sn)_2O$, toluene, reflux; then BnOCOCl, -20°C; then Ac_2O, pyr.
ii) Pd/C, H_2, EtOAc/EtOH.

Scheme 1

(83%) and (7) (94%) were obtained directly. The 6-carbonate (16) was also prepared in this way and isolated as the triacetate (17) in 76% yield (Scheme 1). Hydrogenolysis of this afforded the desired 1,7,8-tri-*O*-acetylcastanospermine (13), and this proved an excellent route for its large scale preparation.

When the alcohol (13) was treated with an excess of DAST two fluorinated products (18) and (19) were formed in a ratio of 5:2. That the major product (18) had undergone a displacement with retention of configuration was ascertained from its ^1H n.m.r. spectrum. The fluorine atom was strongly coupled to H-6 ($J_{6,F}$=51.5 Hz), and the ^1H, ^1H coupling constants ($J_{5ax,6}$=$J_{6,7}$=9.3 Hz) are comparable with those for the parent triacetate (13) ($J_{5ax,6}$=10.5 Hz, $J_{6,7}$=9.3 Hz) and indicate that H-6 is still diaxial to both H-5ax and H-7. In contrast H-6 of 6-epicastanospermine, being equatorial, has only weak coupling ($J_{6,7}$=3 Hz, $J_{5,6}$=1 Hz)[40]. The structure of the more polar fluoride (19) was established by examination of its n.m.r. spectra including ^1H-^1H and ^1H-^{13}C COSY correlations which established the connectivity of the pyrrolizidine ring structure. The α-orientation of the CH_2F group was suggested by comparison of its $J_{2,3}$ value (8.6 Hz) with that of tetra-*O*-acetylaustraline (20) ($J_{2,3}$=8.8 Hz) and its 3-epimer (21)



Scheme 2

($J_{2,3}$=5.4 Hz)[41,42]. The structure of (19) was confirmed by x-ray crystallography. Formation of these products can be rationalised by invoking participation of the nitrogen in the displacement. Thus the DAST ester (22) suffered an intramolecular displacement affording the aziridinium ion intermediate (23) which was then attacked by fluoride ion to give fluorides (18) and (19) (Scheme 2). An analogous participation of the ring nitrogen in displacements at an adjacent centre has been previously observed for a swainsonine derivative where an aziridinium ion intermediate was also invoked[43].* Deacetylation of triacetate (18) gave 6-deoxy-6-fluorocastanospermine (24) which had m.p. and ^1H and ^{13}C n.m.r. spectra in agreement with material obtained by total synthesis[44]. In the same way (19) afforded the interesting analogue (25) of the naturally occurring glycosidase inhibitor australine.

In order to explore further substitutions at C-6 the 6-hydroxy compound (13) was converted to the stable crystalline mesylate (26). Heating of this mesylate with sodium azide in DMSO gave a separable mixture of the castanospermine and australine azides (27) and (28) in a 2:1 ratio implying that the aziridinium ion (23) is again an intermediate. Recently Merrell Dow workers have reported that treatment of the very similar mesylate (29) (synthesized in 9 steps from castanospermine) with sodium iodide in methyl ethyl ketone followed by sodium azide in DMF generated the azide (30), but no mention was made of any rearrangement product[45]. When our mesylate (26) was allowed to react with sodium iodide in refluxing methyl ethyl ketone only the product (31) of retained configuration was obtained. Treatment of this iodide (31) with sodium azide in DMF afforded the same two azides (27) and (28) in the same ratio that had been obtained directly from the mesylate. Reduction of azide (27) gave the amine (32) which was deacetylated affording 6-amino-6-deoxycastanospermine (33), or *N*-acetylated, affording (34), and then *O*-deacetylated to give the known[45] amide (35). Reduction of the australine azide (28) gave 8-acetamido-1,7-di-*O*-acetyl-8-deoxyaustraline (36), the product of acetyl migration from oxygen to nitrogen. O-Deacetylation of this afforded amide (37).

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* Participation by the adjacent (C-7) acetate could also lead to products of displacement with retention, but this route could not give rise to australine analogues, and, in any case displacement with retention occurs when there is a non-participating group at C-7 (*vide infra*).

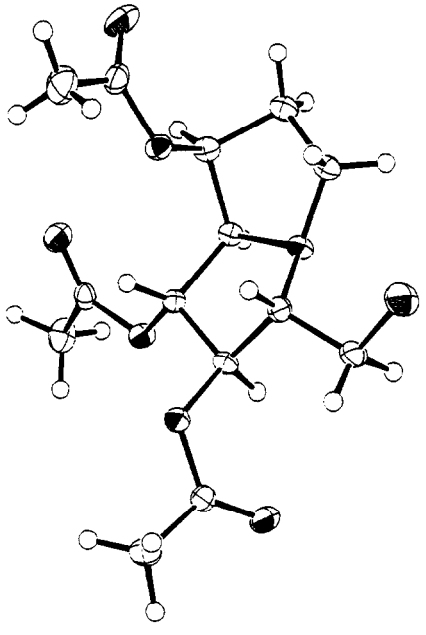


Figure 1. ORTEP drawing of (19)

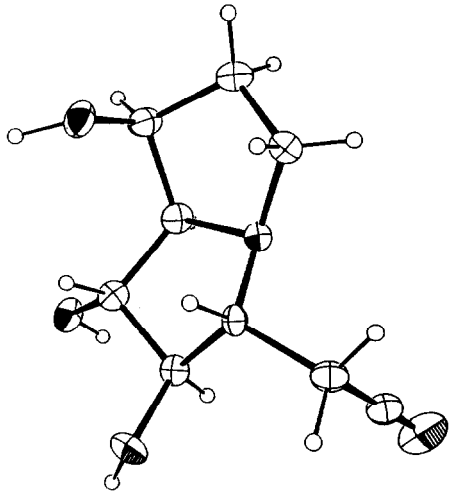
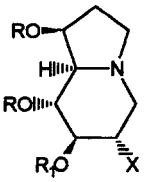


Figure 2. ORTEP drawing of (43)

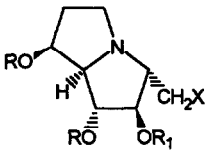
In further displacement reactions applied to mesylate (26), treatment with tetraethylammonium chloride gave a 10:1 mixture of the castanospermine and australine chlorides (38) and (39), whereas with tetrabutylammonium bromide only the unrearranged bromide (40) was obtained. Deacetylation of chloride (38) afforded 6-chloro-6-deoxycastanospermine (41). With potassium cyanide in methanol, mesylate (26) gave a separable mixture of 6-cyano-6-deoxycastanospermine (42) and 8-cyano-8-deoxyaustraline (43) in moderate yield together with a small amount of epoxide (44). The structure of the australine nitrile (43) was confirmed by x-ray crystallography.

Epoxide (44) was also synthesized by stirring mesylate (26) in a suspension of sodium hydroxide in DMF. Upon acid hydrolysis this epoxide underwent diaxial opening to give 6,7-diepicastanospermine (45), which has recently been isolated as a minor alkaloid from the seeds of *Castanospermum australe*[46]. The ^{1}H n.m.r. spectra of (45) and its tetraacetate (46) were consistent with them having inverted stereochemistry at C-6 and C-7 with respect to castanospermine. Thus the equatorially disposed H-6 of compound (45) is only weakly coupled to H-5_{ax} and H-5_{eq} (J<1 Hz), and H-7 (also equatorial) is only moderately coupled to H-8 (J=3 Hz). In compounds with castanospermine stereochemistry, where H-6 and H-7 are both axial, coupling is much stronger, typically $J_{5ax,6}$ = 10.5 Hz and $J_{7,8}$ = 9 Hz.

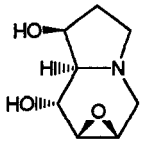
In a further displacement reaction, mesylate (26) was treated with sodium formate in DMSO at 80°C to give a good yield of castanospermine and australine formates (47) and (48) in a ratio of 3:2. The australine formate (48) was selectively deformylated (NH_4OH, MeOH) to give 1,2,7-tri-*O*-acetylaustraline (49). This compound was glucosylated by treatment with penta-*O*-acetyl-β-D-glucopyranose in the presence of trimethylsilyl triflate to give the peracetylated β-glucoside (50). Traces of the α-glucoside (51) and tetraacetyl australine (20) were also formed. Zemplen deacetylation of (50) gave glucoside (52).



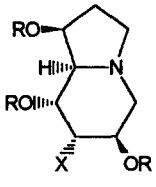
(26) R=R_1=Ac, X=OMs
(27) R=R_1=Ac, X=N_3
(29) R=Ac, R_1=Bz, X=OMs
(30) R=Ac, R_1=Bz, X=N_3
(31) R=R_1=Ac, X=I
(32) R=R_1=Ac, X=NH_2
(33) R=R_1=H, X=NH_2
(34) R=R_1=Ac, X=NHAc
(35) R=R_1=H, X=NHAc
(38) R=R_1=Ac, X=Cl
(40) R=R_1=Ac, X=Br
(41) R=R_1=H, X=Cl
(42) R=R_1=H, X=CN
(47) R=R_1=Ac, X=OCHO
(54) R=R_1=Ac, X=OTf
(55) R=R_1=Ac, X=OBn
(57) R=R_1=H, X=OBn
(58) R=R_1=H, X=OMs
(59) R=R_1=H, X=OMe
(75) R=R_1=H, X=N(Ac)Bn
(78) R=R_1=Ac, X=NEt_2



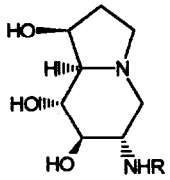
(28) R=R_1=Ac, X=N_3
(36) R=Ac, R_1=H, X=NHAc
(37) R=R_1=H, X=NHAc
(39) R=R_1=Ac, X=Cl
(43) R=R_1=H, X=CN
(48) R=R_1=Ac, X=OCHO
(49) R=R_1=Ac, X=OH
(50) R=R_1=Ac, X=O-β-D- Glucopyranosyl Tetraacetate
(51) R=R_1=Ac, X=O-α-D- Glucopyranosyl Tetraacetate
(52) R=R_1=H, X=O-β-D- Glucopyranosyl
(53) R=R_1=H, X=OH
(56) R=R_1=Ac, X=OBn
(79) R=R_1=Ac, X=NEt_2



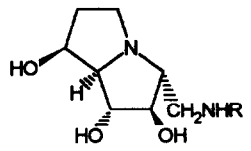
(44)



(45) R=H, X=OH
(46) R=Ac, X=OAc
(76) R=H, X=NHR_1



(60) R=Me
(61) R=Allyl
(63) R=^{n}Butyl
(65) R=2-Methylpropyl
(67) R=1-Methylpropyl
(69) R=1-Methylbutyl
(71) R=2-Methoxyethyl
(73) R=Benzyl



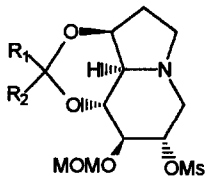
(62) R=Allyl
(64) R=^{n}Butyl
(66) R=2-Methylpropyl
(68) R=1-Methylpropyl
(70) R=1-Methylbutyl
(72) R=2-Methoxyethyl
(74) R=Benzyl

The naturally occurring glycosidase inhibitor australine (53) becomes available from this route *via* triacetate (49). In an attempt to improve the overall yield of australine an alternative procedure was tried. Alcohol (13) was treated with trifluoromethanesulfonic anhydride and 2,6-di-*t*-butyl-4-methylpyridine, and the resulting unstable triflate (54) was reacted *in situ* with excess benzyl alcohol to give only a moderate yield of benzyl ethers (55) and (56), but with the australine isomer (56) the major product. Catalytic debenzylation of (56) gave the australine triacetate (49), which was deacetylated to the natural product (53) isolated as its crystalline hydrochloride. Zemplen deacetylation of (55) gave 6-O-benzylcastanospermine (57).

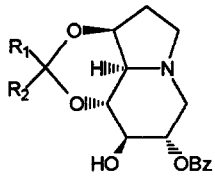
The mesylate (26) could be deacetylated to triol (58) under Zemplen conditions (NaOMe/MeOH/THF), but it was too unstable to be isolated and was instead used *in situ* as a substrate for other nucleophilic displacements. Thus heating mesylate (58) in the solution in which it was formed gave 6-*O*-methylcastanospermine (59) in good yield, and the same treatment in the presence of a variety of primary amines gave moderate yields of 6-alkylamino-6-deoxycastanospermines and 8-alkylamino-8-deoxyaustralines (60) - (74) along with traces of the 6-methyl ether (59) and the 7-alkylamino-7-deoxy-6,7-di-epi-castanospermines (76) - presumably formed *via* epoxide (44). Separation of the products by silica gel chromatography was difficult and the yields of purified products were generally poor. 6-Benzylamino-6-deoxycastanospermine (73) could not be separated from impurities and was acetylated affording a separable mixture of peracetates. *O*-Deacetylation then gave 6-*N*-benzylacetamido-6-deoxycastanospermine (75). This compound generated unusual n.m.r. spectra in that each carbon and proton gave rise to a split or broadened signal, presumably arising from hindered rotation around the *N*-(C=O) amide bond.

A number of *N,N*-disubstituted 6-amino-6-deoxycastanospermine derivatives were required for biological studies. Attempts to synthesize these directly from mesylate (58) led to decomposition of the starting material. However, when triflate (54) was allowed to react with excess diethylamine, a good yield of castanospermine and australine amines (78) and (79) were obtained, but in a 1:6 ratio. Therefore a more efficient route to the required castanospermine amines was sought. It was anticipated that the conformational restriction imposed by a 1,8-cyclic acetal ring, such as in (80), might affect the amount of rearrangement occurring upon reaction with nucleophiles.

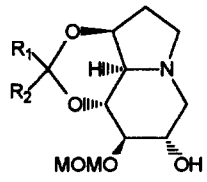
All attempts to form cyclic acetals (isopropylidene or cyclohexylidene) from castanospermine itself were unsuccessful. All the standard conditions returned only starting material unchanged. However, the 6-benzoate (7) readily formed the 1,8-*O*-isopropylidene and cyclohexylidene derivatives (81) and (82). It is not clear why there is such a difference in reactivity between castanospermine and its 6-benzoate. The 6,7-dibenzoate (5) is also readily converted into its 1,8-*O*-cyclohexylidene and isopropylidene derivatives[36]. The alcohols (81) and (82) were transformed into their 7-*O*-MOM ethers and then saponified to the 6-alcohols (83) and (84) respectively. Mesylation then afforded the desired compounds (80) and (85).



(80) R_1=R_2=Me
(85) R_1,R_2=$(CH_2)_5$

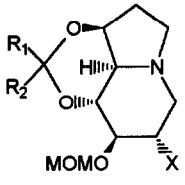


(81) R_1=R_2=Me
(82) R_1,R_2=$(CH_2)_5$

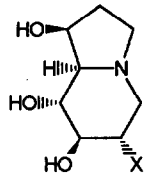


(83) R_1=R_2=Me
(84) R_1,R_2=$(CH_2)_5$

Treatment of mesylate (80) with sodium azide in hot DMSO gave a single compound (86), the product of substitution with retention of configuration. Its structure was demonstrated by acid hydrolysis followed by acetylation to afford the same triacetate azide (27) obtained previously. No product of rearrangement to the corresponding australine derivative was detected. Under the same conditions the cyclohexylidene mesylate (85) also gave only one azide (87), and in a better overall yield (66% from the 6-benzoate (82)). Catalytic hydrogenation of azides (86) or (87) to the 6-amines followed by *N*-acylation and acid hydrolysis gave the 6-*N*-butyryl- and benzoyl-6-deoxycastanospermines (88) and (89). This route also offers improved access to the *N*-acetate (35). Mesylate (85) was also treated with a variety of secondary amines, and benzylamine, in hot DMSO to give only the products (90) - (93) of displacement with retention of configuration. The diethylamine adduct (93) was subjected to acid hydrolysis and then acetylation to give the same triacetate (78) obtained previously. Acid hydrolysis of these products (90)-(93) gave the corresponding *N*,*N*-dialkyl-6-amino-6-deoxycastanospermines (94)-(96) and a pure sample of the *N*-benzyl derivative (73) obtained previously.



(86) R_1=R_2=Me, X=N_3
(87) R_1,R_2=$(CH_2)_5$, X=N_3
(90) R_1,R_2=$(CH_2)_5$, X=NHBn
(91) R_1,R_2=$(CH_2)_5$, X=$N(CH_2CH_2OH)_2$
(92) R_1,R_2=$(CH_2)_5$, X=N(Et)Bu
(93) R_1=R_2=Me, X=NEt_2
(97) R_1,R_2=$(CH_2)_5$, X=I
(98) R_1,R_2=$(CH_2)_5$, X= CH=CH_2
(100) R_1,R_2=$(CH_2)_5$, X=OBu



(88) X=NHCPr (O)
(89) X=NHBz
(94) X=$N(CH_2CH_2OH)_2$
(95) X=N(Et)Bu
(96) X=NEt_2
(99) X= CH=CH_2
(101) X=OBu

When mesylate (85) was treated with Grignard reagents in attempts to effect displacements at C-6, the only reaction observed was O-S cleavage of the sulfonate group with regeneration of alcohol (84). The iodide (97), however, (obtained by iodide displacement on mesylate (85)) reacted readily with vinyl magnesium bromide to give the derivative (98) which after acid hydrolysis afforded 6-deoxy-6-*C*-vinylcastanospermine (99). Alkylation of 6-alcohol (84) with n-butyl bromide (KH/DMSO) afforded the butyl ether (100) in moderate yield, which was deprotected by acid hydrolysis to give 6-*O*-butylcastanospermine (101).

All attempts to oxidise triacetate alcohol (13) to the corresponding 6-ketone were unsuccessful, returning only either starting material alone or no discrete product. However alcohol (84) was successfully oxidised to ketone (102) under Swern conditions. Addition of vinyl magnesium bromide to this ketone gave a major adduct (103) in 74% yield, the stereochemistry of which was resolved by x-ray crystallography. The 6-*C*-methyl branched derivative (104) was also obtained in the same way. Acid hydrolysis then afforded the 6-epi-6-*C*-vinyl-and methyl-castanospermines (105) and (106).

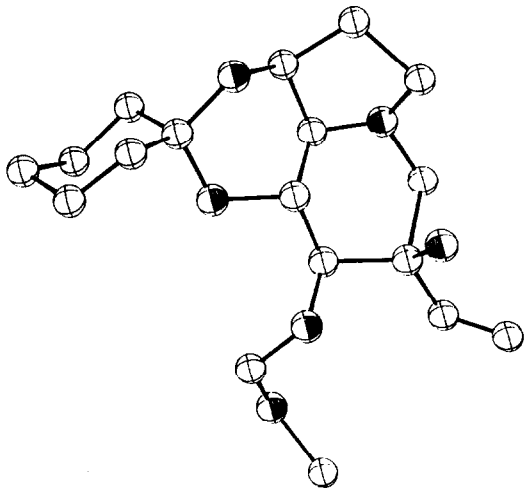
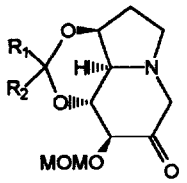
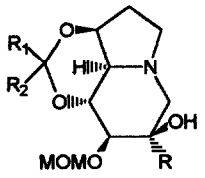


Figure 3. ORTEP drawing of (103)

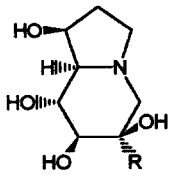
Reduction of ketone (102) with sodium borohydride gave a mixture of alcohols (84) and (107) in which the 6-*epi*- alcohol (107) predominated. Because this mixture was not separable, an alternative route to 6-*epi*-castanospermine was sought. Silylation of alcohol (82) proceeded smoothly affording the fully protected compound (108), but on saponification of the 6-benzoate ester not only the expected 6-alcohol (109) but also the 7-alcohol (110) was obtained - the latter resulting from migration of the silyl group. A one-pot Swern oxidation-borohydride reduction of 6-alcohol (109) gave a separable mixture of 6-*epi*-alcohol (111) and starting material in a ratio of 2:1. Acidic hydrolysis of (111) gave 6-*epi*-castanospermine (112).



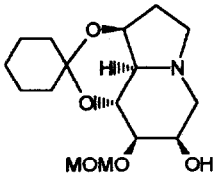
(102)



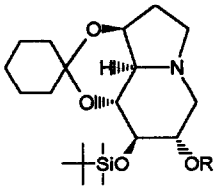
(103) R= CH=CH$_2$
(104) R=Me



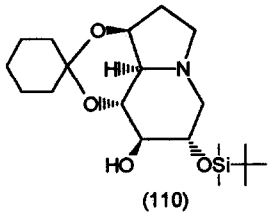
(105) R= CH=CH$_2$
(106) R=Me



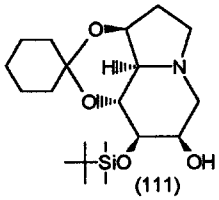
(107)



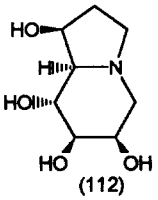
(108) R=Bz
(109) R=H



(110)



(111)



(112)

The results presented here outline efficient routes to a number of selectively protected castanospermine derivatives. The synthesis of castanospermine derivatives modified at C-6 has been explored, an interesting rearrangement to australine-type structures discovered, and ways to avoid this rearrangement delineated. The results of biological testing of these compounds will be reported separately.

X-RAY SINGLE CRYSTAL ANALYSES

The intensity data were collected on a Nicolet R3m diffractometer using graphite-monochromatized MoKα radiation (λ = 0.71073Å) at low temperature by the ω scanning method. Preliminary refinement of the cell parameters was carried out using 22-24 reflections centred automatically in the $6 \leq 2\theta \leq 35°$ range. Crystal and experimental details are summarized in Table 1. Crystal and diffractometer stability was monitored using the intensities of three reflections every 100 reflections. For all crystals, the relative intensities of the standard reflections varied less than 0.5%. Equivalent reflections were averaged and corrected for Lorentz and polarisation factors. No absorption corrections were applied.

The structures were solved by direct methods using programmes SHELXS[47] and SOLVER (NRCVAX)[48], and subsequent difference Fourier syntheses for the hydrogen atoms. Conventional full matrix least squares refinement was performed with anisotropic and isotropic thermal parameters for non-hydrogen and

Table 1: Crystal data, intensity data collection and structural refinement summary for compounds (19) (43) and (104).

	19	43	104
Chemical formula	$C_{14}H_{20}FNO_6$	$C_9H_{14}N_2O_3$	$C_{18}H_{29}NO_5$
Molecular weight	317.32	198.22	339.20
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a Å	8.197(3)	6.256(3)	17.68(4)
b Å	10.426(3)	11.388(6)	16.95(4)
c Å	17.998(5)	13.401(9)	5.948(9)
V Å^3	1538.1(9)	954.8(10)	1782(6)
Z	4	4	4
D_c (g.cm^{-3})	1.370	1.378	1.265
Specimen size, mm	0.28 x 0.43 x 0.48	0.22 x 0.22 x 0.44	0.5 x 0.1 x 0.1
μ, cm^{-1}	1.24	1.13	0.99
Temperature of Collection (°K)	173	190	193
Scan speed ° min $^{-1}$	3.9	4.0	7.3
h range	0 - 10	0 - 8	0-18
k range	0 - 12	0 - 15	-17 - 0
l range	0 - 22	0 - 18	0 - 6
θ range (°)	2 - 26	15 - 29	3 - 22
No. of measured reflections	1832	1562	1303
Conditions for obs.	$I > 3\sigma$ (I)	$I > 2.5\sigma$ (I)	$I > 2.5\sigma$ (I)
No. of refining reflections	1405	792	534
No. of refining parameters	279	184	96
g weighting factor	0.0000	0.0004	0.0006
Secondary Extinction parameter	0.0	0.6(2)	0
R	0.0325	0.0517	0.148
R_w	0.0325	0.0507	0.141

hydrogen atoms respectively, using programmes SHELX76[49] and LSTSQ[48]. The weighting of each reflection was $[\sigma^2 + g\,(F)^2]^{-1}$ (see Table 1).

EXPERIMENTAL

N.m.r. spectra were recorded on a Bruker AC-300 instrument at 300 MHz or 75 MHz (^{13}C) with internal TMS as reference. High-resolution accurate mass determinations were performed on a VG70-250S mass spectrometer under chemical ionisation conditions using isobutane or ammonia as the ionising gas. Melting points were determined on a Reichert hot stage microscope and are uncorrected. Elemental

analyses were performed by the Campbell Microanalytical Laboratory, Dunedin. Silica gel backed aluminium sheets (Merck or Reidel de Haen) were used for thin layer chromatography. Column chromatography was performed on silica gel (230-400 mesh, Merck). Chromatography solvents were distilled prior to use, 'hexanes' refers to a petroleum fraction boiling around 68°C. Castanospermine was obtained as described in the discussion. Tetrahydrofuran was distilled from sodium/benzophenone under argon and dichloromethane was distilled from calcium hydride before use. All other chemicals were commercially available and were used without further purification.

6-O-Benzoylcastanospermine (7). Bis(tributyltin) oxide (108 ml, 0.212 mol) was added to a suspension of castanospermine (20 g, 0.106 mol) in toluene (600 ml) and the mixture was heated under reflux with azeotropic removal of water for 2 hours. The resulting clear solution was cooled under argon to - 10°C and benzoyl chloride (22.1 ml, 0.19 mol) was added slowly with stirring keeping the reaction temperature ≤ 0°C. Stirring was continued overnight while the reaction mixture was allowed slowly to come to room temperature. The toluene was then removed *in vacuo*, the solid residue was shaken with a mixture of 1% aqueous acetonitrile (500 ml) and hexanes (500 ml), filtered and washed thoroughly with petroleum ether. The white solid was dried affording 29.2 g (94%) of 6-*O*-benzoylcastanospermine (7). Recrystallised from aqueous methanol it had m.p. 212-214°C. Lit.[33] m.p. 233 - 236°C. The ^{1}H n.m.r. data was the same as that reported[33].

1,6,7,8-Tetra-*O*-acetylcastanospermine (14). Acetic anhydride (200 ml, excess) was added to a stirred suspension of castanospermine (30 g, 160 mmol) in pyridine (200 ml) at 0°C. The suspension was stirred and warmed to room temperature overnight whereupon it became homogeneous and t.l.c. examination showed that reaction was complete. Solvents were removed by evaporation under reduced pressure and the resulting syrup taken up in CH_2Cl_2 and eluted through a short column of silica gel with hexanes-ethyl acetate (1:1). Recrystallisation from this solvent mixture and further column chromatography and crystallisation of the mother liquors gave the title compound (47 g, 0.13 mol, 85%). Accurate mass, calc for $C_{16}H_{24}NO_8$ (MH^+) 358.1502; obs 358.1499. M.p. 115-116°C. ^{1}H n.m.r. ($CDCl_3$) 5.35 (m H-1) 5.20 (bt J=9.0 H-8) 5.08 (m 2H H-6, H-7) 3.39 (dd J=4.3, 10.5 H-5) 3.22 (m H-3) 2.39-2.19 (m 3H H-2, H-3′, H-8a) 2.09 (m, H-5′) 2.04, 2.02, 2.01, 1.98 (s 3H each, acetate) 1.85 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 170.6, 170.5, 169.9, 169.7 acetate; 75.3 C-6 or C-7; 71.1 C-1; 70.3 C-6 or C-7; 68.5 C-8; 68.3 C-8a; 52.9 C-5; 52.0 C-3; 31.7 C-2; 21.0 20.8, 20.7, 20.7 acetate.

1,7,8 Tri-*O*-acetylcastanospermine (13) and 1,6,8-Tri-*O*-acetylcastanospermine (15). A solution of tetra-acetyl castanospermine (14) (21 g, 60 mmol) and tributyltin methoxide (26 ml, 29.9 g, 93 mmol, 1.6 eq) in tetrahydrofuran (150 ml) was heated under reflux under argon. Monitoring of the reaction by t.l.c. (ethyl acetate) showed transformation of the starting material into two major, less mobile, products (13) and (15), which appeared to slowly degrade to several minor products. The reaction was stopped after 48 hr when the amount of major products appeared to be at a maximum. The solvent was removed under reduced pressure and the residue partitioned between acetonitrile and hexanes. The acetonitrile phase was washed twice with hexanes and then concentrated under reduced pressure. Column chromatography using hexanes-ethyl acetate mixtures as eluent and recrystallisation from these same solvents gave triacetates (13) (5.7 g, 18 mmol, 30%) and (15) (3.2 g, 10.2 mmol, 17%) and also starting material (14) (2.1 g, 6 mmol, 10%). For (13) m.p. 166-168°C. Accurate mass, calc for $C_{14}H_{22}NO_7$ (MH^+) 316.1396; obs. 316.1398. ^{1}H n.m.r. ($CDCl_3$) 5.37 (m H-1) 5.17 (t J=9.5 H-8) 4.84 (t J=9.3 H-7) 3.93 (m H-6) 3.34 (dd J=10.8, 5.2 H-5) 3.23 (m H-3) 2.55 (m OH) 2.45-2.20 (m 3H H-8a, H-2, H-3′) 2.11 (bt J=10.5 H-5′) 2.09 (s 3H acetate) 2.04, 1.98 (s 3H each, acetate) 1.85 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 171.8, 170.6, 169.8 acetate; 79.2 C-7; 71.2 C-1; 79.6 C-6; 68.7 C-8a; 68.1 C-8; 56.2 C-5; 52.0 C-3; 31.6 C-2; 21.0, 20.9, 20.7 acetate. Analysis $C_{14}H_{21}NO_7$ req. C 53.33, H 4.44, N 6.67; found C 53.56, H 4.41, N 6.53. For (15) m.p. 131-133°C. Accurate mass, calc for $C_{14}H_{22}NO_7$ (MH^+) 316.1396, obs 316.1397. ^{1}H n.m.r. ($CDCl_3$) 5.37 (m H-1) 5.07 (bt, J=9.4, H-8) 4.97 (td, J=9.6, 5.3, H-6) 3.57 (td J=9.2, 6.4 H-7) 3.35 (dd, J=10.4, 5.2 H-5) 3.21 (m, H-3) 2.51 (d, J=6.4, OH) 2.40-2.15 (3H, m, H-8a, H-2, H-3′) 2.09, 2.06 (3H, s, each acetate) 2.00-2.04 (4H, m, H-5′, acetate) 1.85 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 171.0, 170.8, 170.6, acetate; 76.0 C-7; 72.9 C-6; 71.3 C-1; 70.6 C-8; 68.5 C-9; 52.9 C-5; 52.0 C-3; 31.6 C-2; 21.1, 21.1, 20.7 acetate. Analysis $C_{14}H_{21}NO_7$ req. C 53.33, H 4.44, N 6.67; found C 53.33, H 4.44, N 6.57.

1,7,8-Tri-*O*-acetylcastanospermine (13). (Alternative method). **(i) 1,7,8-Tri-*O*-acetyl-6-*O*-carboxybenzylcastanospermine (17).** A suspension of castanospermine (20.0 g, 105 mmol) and bis(tributyltin)oxide (140 g, 2.2 eq) in toluene (500 ml) was refluxed for 3 hr under argon with azeotropic removal of water. The resulting solution was cooled to approximately -20°C, benzyl chloroformate (95%) (26 ml, 31.3 g, 1.7 eq) was added, and then stirred at room temperature for 2 hr. Water (20 ml) was added and after further stirring (2 hr) the precipitate of crude 6-*O*-carboxybenzoylcastanospermine (16) was isolated by filtration. This white solid was dried at room temperature under reduced pressure and then taken up in pyridine (200 ml). Acetic anhydride (200 ml) was added at 0°C and the solution was stirred at room temperature overnight and then concentrated to a small volume under reduced pressure. The resulting slurry was taken up in dichloromethane, washed with saturated aqueous sodium bicarbonate and brine, dried ($MgSO_4$) and concentrated under reduced pressure. Recrystallisation from hexanes-ethyl acetate gave (17) (35.9 g, 76%). Accurate mass, calc. for $C_{22}H_{28}NO_9$ (MH^+) 450.1764; obs 450.1763. ^1H n.m.r. ($CDCl_3$) 7.35 (5H s Ph) 5.36 (m H-1) 5.19 (t J=9.3 H-8) 5.15, 5.14 (2H CH_2Ph) 5.07 (t J=9.3 H-7) 4.96 (td J=9.8, 5.2 H-6) 3.45 (dd J=10.5, 5.2 H-5) 3.23 (m H-3) 2.40-2.13 (4H m H-2, H-3′, H-5′, H-8a) 2.04, 1.96, 1.92 (s 3H each, acetate) 1.88 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 170.5, 170.3, 169.8 acetate; 154.2 (C=O)OBn; 134.9, 128.6, 128.3 phenyl; 75.0 C-7; 73.7 C-6; 71.0 C-1; 69.9 C-8; 68.4 C-8a; 68.2 CH_2Ph; 52.8 C-5; 51.9 C-3; 31.6 C-2; 21.0, 20.7, 20.6 acetate.

(ii) 1,7,8-Tri-*O*-acetylcastanospermine (13). To a solution of (17) (18 g, 40 mmol) in ethyl acetate (200 ml) was added ethanol (200 ml) and palladium-on-charcoal (5%, 1 g). The mixture was shaken under hydrogen (60 psi) overnight. Filtration, extractive work up and crystallisation from hexanes-ethyl acetate gave (13) (9.2 g, 73%).

1,7,8-Tri-*O*-acetyl-6-deoxy-6-fluorocastanospermine (18) and 1,2,7-tri-*O*-acetyl-8-deoxy-8-fluoro australine (19). A stirred solution of alcohol (13) (1.0 g, 3.2 mmol) in dichloromethane (10 ml) was cooled in a dry ice-acetone bath. Diethylaminosulphur trifluoride (DAST, 0.9 ml, 2.2 eq) was added and the solution was warmed to reflux for 2 h and then cooled and quenched cautiously with water. Extractive work up and column chromatography using hexanes-ethyl acetate (1:1) as eluent gave the title compounds (18) (0.50 g, 1.6 mmol, 49%) and (19) (0.19 g, 0.64 mmol, 19%) which were further purified by crystallisation from hexanes-ethyl acetate. For (18) m.p. 116-119°C. Accurate mass, calc. for $C_{14}H_{21}FNO_6$ (MH^+) 318.1353, obs 318.1382. ^1H n.m.r. ($CDCl_3$) 5.37 (m H-1) 5.15 (m 2H H-7, H-8) 4.70 (dtd J=5.6, 9.3, 51.5 H-6) 3.46 (ddd J=1.8, 5.6, 10.5 H-5) 3.24 (bt J=7.5 H-3) 2.43-2.26 (m 4H H-2, H-3′, H-5′, H-8a) 2.08, 2.04, 1.98 (s 3H each, acetate) 1.86 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 170.4, 169.8 acetate; 87.6 (d J=180.9 C-6) 75.9 (d J=19.2 C-7) 70.9, 68.4 C-1, C-8a; 67.6 (d J=10.3 C-8) 53.3 (d J=15.6 C-5) 51.9 C-3; 31.7 C-2; 21.0, 20.8, 20.7 acetate. Analysis calc. for $C_{14}H_{20}FNO_6$ C 52.99, H 6.35, N 4.41, F 5.99; found C 53.00, H 6.09, N 4.38, F 5.76. For (19) m.p. 75-77°C. Accurate mass, calc. for $C_{14}H_{21}FNO_6$ (MH^+) 318.1353, obs. 318.1354. ^1H n.m.r. (C_6D_6) 5.63 (t J=8 H-2) 5.55 (t J=7.3 H-1) 5.19 (td J=1.6, 4.2 H-7) 4.29 (ddd J=4.0, 9.3, 47.2 H-8) 4.27 (ddd J=6.2, 9.3, 47.6 H-8′) 3.41 (dd J=4.4, 6.3 H-7a) 3.09 (dddd, J=3.9, 6.2, 8.6, 16.2 H-3) 2.94 (t J=7.8 H-5) 2.48 (td J=6.2, 10.2 H-5′) 1.72 (m 4H acetate, H-6) 1.67, 1.65 (s 3H each, acetate) 1.57 (m H-6′). ^{13}C n.m.r. (C_6D_6) 170.2, 169.7, 169.2 acetate, 85.1 (d J=71.0 C-8) 78.1 (d J=7.6 C-2) 74.1 C-1; 73.4 C-7; 69.8 C-7a; 68.2 (d J=19.4 C-3) 52.3 C-5; 34.0 C-6; 20.6, 20.4 acetate. Analysis $C_{14}H_{20}FNO_6$ req. C 52.99, H 6.35, N 4.41, F 6.00; found C 53.06, H 6.30, N 4.27, F 5.87.

6-Deoxy-6-fluorocastanospermine (24). Triacetate (18) (0.50 g, 1.58 mmol) was dissolved in methanol saturated with ammonia. After stirring at room temperature overnight the solvent was removed under reduced pressure and the residue crystallised from ethyl acetate affording (24) (0.2 g, 1.05 mmol, 66%). M.p. 142-147°C (Lit. [44] m.p. 142-143°C). Accurate mass, calc. for $C_8H_{15}FNO_3$ (MH^+) 192.1036; obs. 192.1029. ^{13}C n.m.r. (D_2O) 93.5 (d J=175.7 C-6) 79.7 (d J=17.2 C-7) 73.7, 72.0 C-1, C-8a; 70.9 (d J=11.2 C-8) 55.3 (d J=26.1 C-5) 54.2 C-3; 35.5 C-2.

8-Deoxy-8-fluoroaustraline (25). Triacetate (19) (0.22 g, 0.69 mmol) was dissolved in methanol saturated with ammonia. After stirring at room temperature overnight the solvent was removed under reduced pressure and the residue chromatographed using dichloromethane-methanol-aqueous ammonium hydroxide (13:4:1) as eluent to give the title compound (25) (0.10 g, 0.52 mmol, 76%). Accurate mass, calc for $C_8H_{15}FNO_3$ (MH^+) 192.1036 obs. 192.1028. ^1H n.m.r. (D_2O) 4.57 (ddd, J=2.4, 10.3, 47.2, H-8) 4.47 (ddd

J=4.8, 10.3, 47.3 H-8′) 4.32 (m H-7) 4.19 (t J=7.8 H-1) 3.97 (bt J=8.9 H-2) 3.13 (dd J=4.3, 7.4 H-7a) 3.07 (m, H-5) 2.79 (dddd J=2.6, 4.6, 9.6, 24.5 H-3) 2.64 (td J=6.2, 10.7 H-5′) 1.81-2.01 (m 2H H-6, H-6′). ^{13}C n.m.r. (D_2O) 85.1 (d J=67.2 C-8) 79.6 (d J=7.7 C-2) 75.5, 73.1, 72.1 C-1, C-7, C-7a; 71.5 (d J=18.7 C-3) 55.8 C-5; 37.6 C-6.

1,7,8-Tri-*O*-acetyl-6-*O*-mesylcastanospermine (26). To a stirred solution of triacetate (13) (15 g, 47.6 mmol) in pyridine (200 ml) cooled in an ice-water bath, was added methanesulphonyl chloride (4.5 ml, 6.7 g, 58.2 mmol, 1.2 eq). The mixture was stirred overnight and then the solvent was removed under reduced pressure. The residue was taken up in dichloromethane and washed with saturated aqueous sodium bicarbonate and then brine. Removal of the solvent under reduced pressure and crystallisation from ethyl acetate-hexanes gave the title compound (26) (16 g, 40.7 mmol, 86%). M.p. 180-182°C. Accurate mass, calc. for $C_{15}H_{24}NO_9S$ (MH^+) 394.1172, obs 394.1167. ^{1}H n.m.r. ($CDCl_3$) 5.37 (m H-1) 5.20 (t J=9.4 H-8) 5.09 (t J=9.3 H-7) 4.80 (td J=9.7, 5.0 H-6) 3.53 (dd J=10.7, 5.5 H-5) 3.25 (m, H-3) 3.01 (3H s mesyl CH_3) 2.40-2.25 (m 4H H-2, H-3′, H-5′, H-9) 2.07, 2.05, 1.98 (s 3H each, acetate) 1.87 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 170.4, 170.2, 169.7, acetate; 76.0 C-6; 74.6 C-7; 70.9 C-1; 68.2 C-8a; 68.0 C-8; 53.9 C-5; 51.8 C-3; 38.1 mesyl CH_3; 31.6 C-2; 21.0, 20.8, 20.7 acetate.

1,7,8-Tri-*O*-acetyl-6-azido-6-deoxycastanospermine (27) and 1,2,7-Tri-*O*-acetyl-8-azido-8-deoxyaustraline (28). A solution of mesylate (26) (1.0 g, 2.5 mmol) and sodium azide (0.5 g, 3 eq) in dimethyl sulphoxide was stirred at 80°C for 1 hr and then at 60°C overnight. Extractive work-up (dichloromethane-water) followed by column chromatography using hexanes-ethyl acetate as eluent gave azides (27) (0.48 g, 1.4 mmol, 56%) and (28) (0.22 g, 0.65 mmol, 25%). For (27): m.p. 135-136°C (ethyl acetate-hexanes). Accurate mass, calc. for $C_{14}H_{21}N_4O_6$ (MH^+) 341.1461, obs. 341.1470. ^{1}H n.m.r. ($CDCl_3$) 5.37 (m H-1) 5.16 (bt J=9.5 H-8) 4.96 (t J=9.5 H-7) 3.77 (td J=10.3, 5.1 H-6) 3.29 (dd J=11.1, 5.1 H-5) 3.24 (m H-3) 2.35-2.21 (3H m H-2, H-3′, H-8a) 2.10 (3H s acetate) 2.04 (4H m acetate, H-5′) 1.98 (3H s acetate) 1.86 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 76.5 C-7; 71.2 C-1; 68.5, 68.5 C-8, C-8a; 60.0 C-6, 53.7 C-5; 52.1 C-3; 31.6 C-2. Analysis $C_{14}H_{20}N_4O_6$ req. C 49.41 H 5.92 N 16.47; found C 49.71 H 5.92 N 16.53. For (28): accurate mass, calc. for $C_{14}H_{21}N_4O_6$: (MH^+) 341.1461, obs. 341.1468. ^{1}H n.m.r. ($CDCl_3$) 5.47 (t J=7.8 H-2) 5.26 (m 2H H-1, H-7) 3.56 (dd J=4.3, 6.2 H-7a) 3.46 (dd J=3.7, 12.7 H-8) 3.25 (m 2H H-5, H-8′) 3.00 (td J=4.3, 8.6 H-6) 2.71 (td J=9.9, 6.8 H-5′) 2.13, 2.09, 2.05 (11H m acetate, H-6, H-6′). ^{13}C n.m.r. ($CDCl_3$) 78.4 C-2; 73.7 73.4 C-1, C-7; 69.5 C-3; 67.8 C-7a; 52.6, 51.7 C-5, C-8; 33.9 C-6.

1,7,8-Tri-*O*-acetyl-6-amino-6-deoxycastanospermine (32). A solution of azide (27) (3.4 g, 10 mmol) in toluene was stirred with palladium-on-carbon (5%, 0.10 g) under hydrogen at atmospheric pressure for 24 hr. The catalyst was removed by filtration and filtrate concentrated under reduced pressure. Column chromatography with dichloromethane-methanol as eluent gave the title compound (32) (2.5 g, 8.1 mmol, 81%) which was recrystallised from hexanes-ethyl acetate. M.p. 151-153°C. Accurate mass, calc. for $C_{14}H_{23}N_2O_6$ (MH^+) 315.1566, obs. 315.1550. ^{1}H n.m.r. ($CDCl_3$) 5.37 (m H-1) 5.14 (t J=9.5 H-8) 4.96 (t J=9.5 H-7) 3.24 (2H m H-3, H-5) 3.11 (td J=4.7, 10.2 H-6) 2.40-2.16 (3H m H-2, H-3′, H-8a) 2.09, 2.05 (s 3H each, acetate) 1.98 (4H m acetate, H-5′) 1.85 (m H-2′) 1.38 (2H bs NH_2). ^{13}C n.m.r. ($CDCl_3$) 79.7 C-7; 71.1 C-1; 68.8, 68.7 C-8, C-9; 57.3 C-5; 51.9 C-3; 51.5 C-6; 31.3 C-2. Analysis, $C_{14}H_{24}N_2O_7$ ($M+H_2O$) req. C 50.60 H 7.28 N 8.43, found C 50.92 H 7.21 N 8.52.

6-Amino-6-deoxycastanospermine (33). Sodium methoxide in methanol (1% sodium, 0.5 ml) was added to a stirred solution of acetylated amine (32) (1g, 3.2 mmol) in dry methanol (20 ml). After 2 hr the solution was run through a column of cation exchange resin (Dowex X12) in the ammonium form. Concentration of the eluate under reduced pressure and column chromatography with dichloromethane-methanol-ammonium hydroxide (aqueous 25% NH_3) (5:4:1) as eluant gave amine (33) (0.45 g, 2.3 mmol, 75%) which was recrystallised from methanol. M.p. 185-190°C (dec). Accurate mass, calc. for $C_8H_{17}N_2O_3$ (MH^+) 189.1239, obs 189.1249. ^{1}H n.m.r. (D_2O) 4.37 (m H-1) 3.88 (t J=9.4 H-8) 3.16 (bt J=9.3 H-7) 3.07 (m 2H H-3, H-6) 2.79 (dd J=4.6, 10.2 H-5) 2.28 (m H-2) 2.15 (q J=8.9 H-3′) 1.97 (m 2H H-5′, H-8a) 1.66 (m H-2′). ^{13}C n.m.r. (D_2O) 81.9 C-7; 74.3 C-8a; 72.3, 72.2 C-1, C-8; 57.8 C-5; 54.5 C-6; 54.3 C-3; 35.3 C-2. Analysis $C_8H_{16}N_2O_3$ req. C 51.06, H 8.57, N 14.89; found C 50.61, H 8.42, N 14.64.

6-Acetamido-1,7,8-tri-*O*-acetyl-6-deoxycastanospermine (34). A solution of amine (32) in pyridine (10 ml) and acetic anhydride (10 ml) was stirred overnight at room temperature. The mixture was evaporated to dryness under reduced pressure and chromatographed on a column using dichloromethane-methanol (9:1) as eluent to give the title compound (34) (1.15 g, 3.2 mmol, 101%) which was recrystallised from ethyl acetate. M.p. 217-219°C. Accurate mass, calc. for $C_{16}H_{25}N_2O_7$ (MH^+) 357.1662, obs. 357.1672. ^1H n.m.r. ($CDCl_3$) 5.90 (d 2H NH2) 5.37 (m H-1) 5.27 (t J=9.5 H-8) 4.82 (dd J=9.4, 10.5 H-7) 4.27 (m H-6) 3.42 (dd J=4.9, 10.8 H-5) 3.23 (m, H-3) 2.39-2.08 (m 4H H-2, H-3′, H-5′, H-8a) 2.06 (s 6H, acetates) 1.98, 1.93 (s 3H each, acetate) 1.85 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 75.7 C-7; 71.2 C-1; 68.8 C-8a; 68.1 C-8; 54.4 C-5; 51.9 C-3; 50.5 C-6; 31.6 C-2. Analysis, $C_{16}H_{24}N_2O_7$ req. C 53.93 H 6.79 N 7.87; found C 53.47 H 6.60 N 7.92.

6-Acetamido-6-deoxycastanospermine (35). Sodium methoxide in methanol (1% sodium, 0.5 ml) was added to a stirred solution of acetylated amine (34) (0.5 g, 1.6 mmol) in dry methanol (10 ml). After a few minutes the solid product (35) was removed by filtration. The filtrate was run through a column of cation exchange resin (Dowex X12) in the ammonium form and the solvent removed under reduced pressure to give further (35). The batches were combined and recrystallised from methanol, (0.36 g, 1.6 mmol, 100%) m.p. 234-236°C. Accurate mass calc. for $C_{10}H_{19}N_2O_4$ (MH^+) 231.1345, obs. 231.1352. ^1H n.m.r. (D_2O) 4.34 (m H-1) 3.78 (td J=4.5, 10.4 H-6) 3.58 (t J=9.2 H-8) 3.30 (t J=9.5 H-7) 3.01 (m, 2H, H-3, H-5) 2.24 (m, H-2) 2.15 (q J=8.7 H-3′) 1.93 (m 5H H-5′, H-8a, acetate) 1.64 (m H-2′). ^{13}C n.m.r. (D_2O) 175.8 acetate; 78.9 C-7; 73.7 C-8a; 72.1, 72.1 C-1, C-8; 55.9 C-5; 54.0 C-3; 53.5 C-6; 35.1 C-2; 24.5 acetate. Analysis $C_{10}H_{20}N_2O_5$ ($M+H_2O$) req. C 48.38 H 8.12 N 11.28; found C 48.56 H 7.93 N 11.13.

8-Acetamido-1,7-di-*O*-acetyl-8-deoxyaustraline (36). A solution of azide (28) (1.6 g, 4.7 mmol) in toluene-ethyl acetate was stirred with palladium-on-carbon (5%, 0.1 g) under hydrogen at atmospheric pressure for 4 hr. The catalyst was removed by filtration and the solvents were evaporated under reduced pressure. Column chromatography with dichloromethane-methanol as eluent gave the title compound (36) (1.3 g, 4.1 mmol, 87%). Accurate mass, calc. for $C_{14}H_{23}N_2O_6$ (MH^+) 315.1566; obs 315.1545. ^1H n.m.r. ($CDCl_3$) 6.35 (bs NH) 5.30 (m H-7) 5.01 (dd J=6.2, 7.7 H-1) 4.05 (dd J=7.9, 9.0 H-2) 3.95 (bs OH) 3.81 (ddd J=2.6, 8.2, 14.2 H-8) 3.40 (dd J=4.1, 6.1 H-7a) 3.12 (m H-5) 3.00 (td J=3.8, 14.2 H-8′) 2.78 (ddd J=2.7, 4.3, 9.0 H-3) 2.61 (m H-5′) 2.11, 2.09, 2.05 (m 11H H-6, H-6′, acetate). ^{13}C n.m.r. ($CDCl_3$) 171.6, 171.5, 170.0 acetate; 77.4 C-2; 76.3 C-1; 73.5 C-7; 69.6 C-3; 69.4 C-7a; 50.7 C-5; 39.2 C-8; 33.8 C-6; 23.1, 21.1, 20.8 acetate.

8-Acetamido-8-deoxyaustraline (37). Sodium methoxide in methanol (1% sodium, 0.5 ml) was added to a solution of amide (36) (0.9 g, 2.9 mmol) in dry methanol (10 ml). After stirring overnight the solvent was removed under reduced pressure and the residue chromatographed using dichloromethane-methanol-ammonium hydroxide (aqueous, 25% NH_3) (5:4:1) as eluent to give amide (37) (0.6 g, 2.6 mmol, 91%) which was recrystallised from methanol-ethyl acetate. Accurate mass, calc. for $C_{10}H_{19}N_2O_4$ (MH^+) 231.1345, obs. 231.1352. ^1H n.m.r. (D_2O) 4.21 (m H-7) 4.16 (t J=7 H-1) 3.81 (t J=8.1 H-2) 3.39 (dd J=2.6, 13.9 H-8) 3.27 (dd J=6.1, 13.9 H-8′) 3.04-3.13 (m 2H H-5, H-7a) 2.63-2.72 (m 2H H-5′, H-3) 1.97 (m 5H H-6, H-6′, acetate). ^{13}C n.m.r. ($CDCl_3$) 177.1 acetate; 83.1 C-2; 75.6 C-1; 73.6 C-7a; 72.1 C-7; 70.9 C-3; 54.2 C-5; 44.3 C-8; 38.0 C-6; 24.7 acetate.

1,7,8-Tri-*O*-acetyl-6-chloro-6-deoxycastanospermine (38). A solution of mesylate (26) (2.5 g, 7.1 mmol) and tetraethylammonium chloride (3.6 g, 21.3 mmol, 3 eq) in acetonitrile (50 ml) was heated at 65°C overnight. Concentration under reduced pressure and chromatography using hexanes-ethyl acetate (2:1, 1:1) as eluent gave the title compound (38) (1.8 g, 5.3 mmol, 76%) and a small amount (0.15 g, 7%) of a compound tentatively identified as the australine isomer (39). Accurate mass, calc. for $C_{14}H_{21}{}^{35}ClNO_6$ (MH^+) 334.1057, obs. 334.1066. ^1H n.m.r. ($CDCl_3$) 5.38 (m H-1) 5.14 (t J=9.4 H-8) 5.03 (t J=9.6 H-7) 4.03 (td J=5.0, 10.5 H-6) 3.43 (dd J=5.0, 11.2 H-5) 3.25 (m, H-3) 2.28-2.40 (m 4H H-2, H-3′, H-5′, H-8a) 2.09, 2.04, 1.98 (s 3H each, acetate) 1.88 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 177.3 C-7; 71.0 C-1; 68.8 C-8; 68.5 C-8a; 57.0 C-5; 55.2 C-6; 51.7 C-3; 31.5 C-2.

1,7,8-Tri-*O*-acetyl-6-bromo-6-deoxycastanospermine (40). A solution of mesylate (26) (1.0 g, 2.5 mmol) and tetrabutylammonium bromide (2.5 g, 7.8 mmol, 3.1 eq) was stirred at 80°C overnight. The solvent was removed under reduced pressure and the residue was triturated with ethyl acetate and then filtered. The filtrate was applied to a column which was eluted with hexanes-ethyl acetate (1:1) to give

the title compound (40) (0.79 g, 2.1 mmol, 83%). M.p.94-95°C. Accurate mass, calc. for $C_{14}H_{21}NO_6{}^{79}Br$ (MH^+) 378.0552, obs. 378.0587. ^1H n.m.r. ($CDCl_3$) 5.38 (m H-1) 5.12 (m 2H H-7, H-8) 4.06 (td J=5.0, 10.5 H-6) 3.48 (dd J=4.9, 11.1 H-5) 3.25 (m H-3) 2.48 (t J=11.2 H-5′) 2.41-2.25 (m 3H H-2, H-3′, H-8a) 2.09, 2.04, 1.97 (s 3H each, acetate) 1.88 (m H-2′). ^{13}C n.m.r. ($CDCl_3$)170.1, 170.1, 169.7 acetate; 77.3 C-7 or C-8; 71.1 C-1; 69.2 C-7 or C-8; 68.5 C-8a; 57.6 C-5; 51.6 C-3; 45.5 C-6; 31.6 C-2; 21.0, 20.7, 20.7 acetate.

6-Chloro-6-deoxycastanospermine (41). A solution of triacetate (38) (1.7 g, 5.1 mmol) in methanol was brought to pH 11 by addition of a solution of sodium methoxide in methanol. Concentration under reduced pressure and chromatography using dichloromethane-ethanol (4:1) as eluent gave the title compound (41) (0.90 g, 4.3 mmol, 85%), which was recrystallised from ethanol. M.p. 173-176°C (dec). Accurate mass, calc. for $C_8H_{15}{}^{35}ClNO_3$ (MH^+) 208.0740, obs. 208.0740. ^1H n.m.r. (D_2O) 4.41 (m H-1) 3.73 (td J=4.9, 10.4 H-6) 3.61 (t J=9.3 H-8) 3.48 (t J=9.3 H-7) 3.35 (dd J=4.9, 11.3 H-5) 3.12 (m H-3) 2.38 (t J=11.2 H-5′) 2.30 (m 2H H-2, H-3′) 2.12 (dd J=4.3, 9.8 H-8a) 1.74 (m H-2′). ^{13}C n.m.r. (D_2O) 81.7 C-7; 73.9 C-8a; 72.2, 72.1 C-1, C-8; 60.9 C-6; 59.1 C-5; 54.0 C-3; 35.3 C-2.

6-Cyano-6-deoxycastanospermine (42) and 8-cyano-8-deoxyaustraline (43). A suspension of mesylate (26) (5.0 g, 13 mmol) and potassium cyanide (2.5 g, 39 mmol, 3 eq) in methanol was stirred at 60°C for 3 hr. The mixture was cooled, filtered and the filtrate concentrated under reduced pressure. Repeated chromatography using dichloromethane-methanol (9:1, 5:1) as eluent gave the title compounds (42) (0.94 g, 4.7 mmol, 37%) and (43) (1.3 g, 6.6 mmol, 51%) and also epoxide (44) (0.26 g, 1.5 mmol, 12%) Nitriles (42) and (43) were recrystallised from methanol-ethyl acetate. (42) M.p. 188-195°C (dec). Accurate mass, calc for $C_9H_{15}N_2O_3$ (MH^+) 199.1083, obs. 199.1083. ^1H n.m.r. (D_2O) 4.39 (m H-1) 3.66 (t J=8.9 H-7 or H-8) 3.54 (td J=1.5, 9.5 H-7 or H-8) 3.31 (dd J=4.2, 11.3 H-5) 3.10 (m H-3) 2.89 (td J=4.0, 11.1 H-6) 2.40 (t J=11.6 H-5′) 2.34-2.19 (m 2H H-2, H-3′) 2.03 (dd J=4.2, 9.6 H-8a) 1.70 (m H-2′). ^{13}C n.m.r. (D_2O) 122.3 CN; 76.9, 73.7, 72.3, 72.6 C-1, C-7, C-8, C-8a; 54.1, 53.3 C-3, C-5; 37.5 C-6; 35.2 C-2. (43) M.p.169-171°C. Accurate mass, calc. for $C_9H_{15}N_2O_3$ (MH^+) 199.1083, obs. 199.1084. ^1H n.m.r. (D_2O) 4.35 (m H-7) 4.21 (t J=8.3 H-1) 3.90 (td J=8.6 H-2) 3.25 (m H-5) 3.22-3.12 (m 2H H-5, H-7a) 2.90-2.63 (m 4H H-3, H-5′, H-8, H-8′) 2.07-1.90 (m 2H H-6, H-6′). ^{13}C n.m.r. (D_2O) 121.6 CN; 83.7 C-2; 74.9 C-1; 73.5 C-7a; 72.1 C-7; 68.2 C-3; 53.7 C-5; 37.6 C-6; 22.8 C-8.

6,7-Anhydro-6-*epi*-castanospermine [(1S, 6R, 7R, 8R, 8aR)-6,7-epoxy-1,8-dihydroxyoctahydroindolizine] (44). A suspension of mesylate (26) (2.0 g, 5.1 mmol) and powdered potassium hydroxide (0.56 g) in dimethylformamide (20 ml) was stirred at room temperature for 24 hr. The mixture was filtered and the filtrate neutralised with acetic acid and concentrated under reduced pressure. Column chromatography using dichloromethane:methanol (6:1, 5:1) as eluent gave the title compound (44) (0.4 g, 2.3 mmol, 46%) which was crystallised from methanol-ethyl acetate. M.p. 135-137°C. Accurate mass, calc. for $C_8H_{14}NO_3$ (MH^+) 172.0974, obs. 172.0975. ^1H n.m.r. (D_2O) 4.37 (m H-1) 4.07 (d J=9.6 H-8) 3.86 (d J=3.9 H-6 or H-7) 3.42 (s H-6 or H-7) 3.40 (d J=13.3 H-5) 3.02 (m H-3) 2.42 (d J=13.1 H-5′) 2.28 (m H-2) 2.21 (q J=9.2 H-3′) 1.91 (dd J=5.3, 9.6 H-8a) 1.59 (m H-2′). ^{13}C n.m.r. (D_2O) 71.9 C-1; 71.2 C-8a; 65.3 C-8; 58.6, 56.1 C-6, C-7; 54.7 C-3; 53.3 C-5; 34.8 C-2.

6,7-Di-*epi*-castanospermine [(1S, 6R, 7S, 8R, 8aR)-1,6,7,8-tetrahydroxyoctahydroindolizine] (45), and 1,6,7,8-tetra-*O*-acetyl-6,7-di-*epi* castanospermine (46). A solution of epoxide (44) (0.49 g, 2.9 mmol) in aqueous sulphuric acid (20 ml, 5%) was stirred overnight at 55°C. The solution was neutralised with anion exchange resin (Amberlyst A-26) in the hydroxide form, filtered and evaporated to dryness under reduced pressure. Column chromatography using dichloromethane-methanol-ammonium hydroxide (aqueous, 25% NH_3), 5:4:1 as eluent gave the title compound (45) (0.30 g, 1.5 mmol, 55%). Accurate mass, calc. for $C_8H_{16}NO_4$ (MH^+) 190.1079, obs. 190.1085. ^1H n.m.r. (D_2O) 4.45 (m H-1) 4.10 (dd J=3.1, 10.2 H-8) 4.04 (m 2H H-6, H-7) 3.15 (m H-3) 3.02 (d J=12.5 H-5) 2.24 (d J=12.5 H-5′) 2.39-2.19 (m 3H H-2, H-5′, H-8a) 1.74 (m H-2′). ^{13}C n.m.r. (D_2O) 73.3, 73.0, 72.4, 68.9, 68.3 C-1, C-6, C-7, C-8, C-9; 54.9, 54.8 C-3, C-5; 34.5 C-2. A portion of (45) was acetylated with pyridine-acetic anhydride. Evaporation of the reagents under reduced pressure and column chromatography using hexanes-ethyl acetate (1:2) as eluent gave (46). Accurate mass, calc. for $C_{16}H_{24}NO_8$ (MH^+) 358.1502, obs. 358.1500. ^1H n.m.r. (C_6D_6) 5.72 (m 2H H-7, H-8) 5.50 (m H-1) 4.99 (d J=2.6 H-6) 3.04 (d J=12.8 H-5) 2.75 (m H-3) 2.37 (dd J=4.9, 9.7 H-8a) 2.20 (dd J=1.9, 12.7 H-5′) 1.82, 1.75, 1.68, 1.49 (s 3H each, acetate) 1.53-1.79

(m 3H H-2, H-2′, H-3′). ^{13}C n.m.r. (C_6D_6) 169.9, 169.6, 169.5, 168.8 acetate; 71.9, 70.1, 68.3, 67.4, 65.5 C-1, C-6, C-7, C-8, C-8a; 52.7, 51.4 C-3, C-5; 31.1 C-2; 20.7, 20.5, 20.4, 20.3 acetate.

1,7,8-Tri-*O*-acetyl-6-*O*-formylcastanospermine (47) and 1,2,7-Tri-*O*-acetyl-8-*O*-formylaustraline (48). A suspension of mesylate (26) (5.0 g, 12.7 mmol) and sodium formate (3.0 g, 35.7 mmol, 2.8 eq) in dimethylsulphoxide (25 ml) was stirred at 70-80°C overnight. The reaction mixture was cooled and partitioned between dichloromethane and water. The nonaqueous phase was dried ($MgSO_4$) and concentrated under reduced pressure. Column chromatography with hexanes-ethyl acetate (1:2, 1:1) as eluent gave the title compounds (47) (2.3 g, 7.6 mmol, 53%) and (48) (1.64 g, 4.8 mmol, 38%). (47) Accurate mass, calc. for $C_{15}H_{22}NO_8$ (MH^+) 344.1352, obs. 344.1335. ^{1}H n.m.r. ($CDCl_3$) 8.02 (s formate) 5.38 (m H-1) 5.24-5.08 (m 3H H-6, H-7, H-8) 3.43 (dd J=4.9, 10.5 H-5) 3.25 (m H-3) 2.42-2.08 (m 4H H-2, H-3′, H-5′, H-8a) 2.05, 2.03, 1.98 (s 3H each, acetate) 1.89 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 170.4, 170.3, 169.6 acetate; 159.6 formate; 74.7, 70.9, 69.7 C-1, C-6, C-7; 68.2, 68.0 C-8, C-8a; 52.4, 51.8 C-3, C-5; 31.5 C-2; 20.9, 20.6, 20.5 acetate. (48). Accurate mass, calc. for $C_{15}H_{22}NO_8$ (MH^+) 344.1345, obs. 344.1335. ^{1}H n.m.r. ($CDCl_3$) 8.11 (s formate) 5.48 (dd J=7.3, 8.6 H-2) 5.29 (m 2H H-1, H-7) 4.30 (dd J=3.6, 11.6 H-8) 4.11 (dd J=4.9, 11.6 H-8′) 3.54 (dd J=4.2, 6.2 H-7a) 3.22 (m H-5) 3.10 (m H-3) 2.70 (m H-5′) 2.13, 2.09, 2.04 (m 11H H-6, H-6′, acetate). ^{13}C n.m.r. ($CDCl_3$) 170.5, 170.0, 169.8 acetate; 160.6 formate; 77.6, 73.6, 73.3, 69.5, 66.7 C-1, C-2, C-3, C-7, C-7a; 63.3 C-8; 51.8 C-5; 33.8 C-6; 21.0, 20.7, 20.7 acetate.

1,2,7-Tri-*O*-acetylaustraline (49). A solution of formate (48) (1.5 g, 44 mmol) in methanol (30 ml) was treated with a solution of ammonium hydroxide in methanol (1.5 M, 1 ml) and stirred at room temperature for 1 hr when t.l.c. showed that no starting material remained. The solution was neutralised with acetic acid and evaporated to dryness under reduced pressure. Column chromatography with ethyl acetate as eluent gave the title compound (49) (1.0 g, 3.2 mmol, 72%). Accurate mass, calc. for $C_{14}H_{22}NO_7$ (MH^+) 316.1396, obs. 316.1400. ^{1}H n.m.r. ($CDCl_3$) 5.50 (dd J=7.3, 8.6 H-2) 5.30 (m 2H H-1, H-7) 3.60 (dd J=3.2, 11.8 H-8) 3.52 (m 2H H-7a, H-8′) 3.17 (m H-5) 2.91 (m H-3) 2.67 (m 2H H-5′, -OH) 2.13, 2.10, 2.04 (m 11H H-6, H-6′, acetate). ^{13}C n.m.r. ($CDCl_3$) 170.6, 170.6, 169.9 acetate; 77.2, 74.1, 73.6, 69.7, 69.6 C-1, C-2, C-3, C-7, C-7a; 59.8 C-8; 51.2 C-5; 33.7 C-6; 21.1, 20.9, 20.8 acetate.

1,2,7-Tri-*O*-acetyl-8-*O*-(tetra-*O*-acetyl-β-D-glucopyranosyl)australine (50). A solution of alcohol (49) (0.80 g, 2.5 mmol), penta-*O*-acetyl-β-D-glucopyranose (1.7 g, 4.3 mmol, 1.7 eq) and trimethylsilyl triflate (1.5 ml, 1.7 g, 7.7 mmol, 3.1 eq) in dichloromethane (10 ml) was added to powdered molecular sieves (4A, 1.0 g) which had been freshly heated over a flame and cooled under argon. The reaction was stirred at room temperature for 72 hr and then filtered and concentrated under reduced pressure. Column chromatography with hexanes-ethyl acetate (1:2) as eluent gave the title β-glucoside (50) (0.50 g, 0.7 mmol, 31%) as well as some α-glucoside and tetraacetylaustraline (20). Accurate mass, calc. for $C_{28}H_{40}NO_{16}$ (MH^+) 646.2347 obs 646.2339. ^{1}H n.m.r. ($CDCl_3$) 5.36-4.99 (m 6H H-1, H-2, H-7, H-2g, H-3g, H-4g) 4.55 (d J=7.9 H-1g) 4.30 (dd J=4.7, 12.3 H-6g) 4.12 (d J=12.0 H-6g′) 3.99 (dd J=2.6, 9.7 H-8) 3.70 (m H-5g) 3.51 (dd J=4.4, 6.0 H-7a) 3.44 (m H-8′) 3.10 (m 2H H-3, H-5) 2.74 (m H-5′) 2.12-2.01 (m 22H H-6, acetate) 1.81 (m H-6′). ^{13}C n.m.r. ($CDCl_3$) 170.6, 170.5, 170.1, 169.8, 169.3, 169.2 acetate; 100.6 C-1g; 77.6 C-2; 73.8, 73.3, 72.7, 3 of C-1, C-7, C-3g, C-4g; 71.9 C-8; 71.7 C-5g; 71.0 C-2g; 69.6 C-7a; 68.2 1 of C-1, C-7, C-3g, C-4g; 67.3 C-3; 61.7 C-6g; 52.4 C-5; 33.8 C-6.

8-*O*-β-D-Glucopyranosylaustraline (52). A solution of acetylated glucoside (50) (0.20 g, 0.31 mmol) in methanol (1.0 ml) was basified with sodium-in-methanol (1% sodium). After 1 hr the white precipitate of the product was removed by filtration affording (52) (0.07 g, 0.20 mmol 64%). Accurate mass, calc. for $C_{14}H_{26}NO_9$ (MH^+) 352.1607, obs. 352.1595. ^{1}H n.m.r. (500 MHz) (D_2O) 4.51 (d J=7.9 H-1g) 4.40 (m H-7) 4.26 (t J=7.8 H-1) 4.14 (dd J=3.3, 10.8 H-8) 4.01 (dd J-8.2, 9.5 H-2) 3.96 (dd J=2.1, 12.5 H-6g) 3.76 (dd J=5.9, 12.5 H-6g′) 3.69 (dd J=6.4, 10.8 H-8′) 3.53 (t J=9.2 H-2g) 3.49 (m H-5g) 3.42 (t J=9.4 H-4g) 3.34 (dd J=7.9, 9.2 H-2g) 3.21 (dd J=4.6, 7.6 H-7a) 3.17 (m H-5) 2.86 (ddd J=3.3, 6.4, 9.5 H-3) 2.76 (td J=6.0, 11.0 H-5′) 2.05 (m H-6) 1.96 (m H-6′). ^{13}C n.m.r. (D_2O) 105.6 C-1g; 81.5 C-2; 78.7 C-5g; 78.4 C-3g; 75.9 C-2g; 75.8 C-1; 73.3 C-7a and C-8; 72.5 C-4g; 72.4 C-7; 71.4 C-3; 63.5 C-6g; 54.4 C-5; 37.8 C-6.

1,7,8-Tri-*O*-acetyl-6-*O*-benzylcastanospermine (55) and 1,2,7-tri-*O*-acetyl-8-*O*-benzylaustraline (56). A solution of alcohol (13) (7.0 g, 22.2 mmol) and 2,6-di-t-butyl-4-methylpyridine (9.0 g, 43.9 mmol, 2.0 eq) in dichloromethane (300 ml) was cooled in ice-water under an argon atmosphere. Trifluoromethanesulfonic anhydride (4.2 ml, 7.1 g, 25.0 mmol, 1.1 eq) was added and the solution stirred for 1 hr. Benzyl alcohol (70 ml, excess) was then added and the solution heated at reflux for 1 hr. Extractive workup (dichloromethane - aqueous sodium hydrogencarbonate) and column chromatography using hexanes-ethyl acetate (4:1, 0:1) as eluent gave the title compounds (54) (crystallised from hexanes-ethyl acetate) (1.8 g, 4.4 mmol, 20%) and (55) (3.2 g, 7.8 mmol, 35%). (54) M.p. 144-147°C. Accurate mass, calc. for $C_{21}H_{28}NO_7$ (MH^+) 406.1866, obs. 406.1851. ^1H n.m.r. ($CDCl_3$) 7.36-7.26 (m 5H aromatic) 5.34 (m H-1) 5.12 (t J=9.5 H-8) 5.03 (t J=9.2 H-7) 4.62 and 4.53 (d J=12.1 CH_2Ph) 3.72 (td J=5.0, 9.7 H-6) 3.34 (dd J=5.1, 10.8 H-5) 3.18 (m H-3) 2.39-2.17 (m 3H H-2, H-5′, H-8a) 2.09 (t J=10.5 H-3′) 2.02, 2.00, 1.97 (s 3H each, acetate) 1.82 (m H-2′). ^{13}C n.m.r. ($CDCl_3$) 137.9, 128.4, 127.8, 127.7 aromatic; 76.8, 75.9, 72.5, 71.1, 68.6, 68.3 C-1, C-6, C-7, C-8, C-8a, CH_2Ph; 53.9, 52.1, C-3, C-5; 31.6 C-2. (55) Accurate mass, calc. for $C_{21}H_{28}NO_7$ (MH^+) 406.1866, obs 406.1856. ^1H n.m.r. ($CDCl_3$) 7.36-7.26 (m 5H aromatic) 5.34 (dd J=7.3, 8.8 H-1 or H-2) 5.25 (m H-1 or H-2, H-7) 4.53 (m 2H CH_2Ph) 3.53 (m 2H H-5, H-8) 3.47 (dd J=5.7, 9.6 H-8′) 3.34 (m H-7a) 3.05 (ddd J=4.3, 5.4, 9.1 H-3) 2.76 (td 7.0, 10.0 H-5′) 2.11 (m 5H H-6, H-6′, acetate) 2.03, 2.00 (s 3H each, acetate). ^{13}C n.m.r. ($CDCl_3$) 138.1, 128.4, 127.7, 127.6 aromatic; 78.3, 74.1, 73.6, 69.7, 67.8 C-1, C-2, C-3, C-7, C-7a; 73.5, 71.6 C-8, CH_2Ph; 52.4 C-5; 33.9 C-6.

6-*O*-Benzylcastanospermine (57). Sodium methoxide in methanol (1% sodium, 1 ml) was added to a suspension of triacetate (54) (0.93 g, 2.3 mmol) in methanol (10 ml). After stirring overnight the solvent was evaporated under reduced pressure and the residue chromatographed using dichloromethane-methanol (9:1) as eluent. Crystallisation from methanol gave the title compound (57) (0.53 g, 1.9 mmol, 82%). M.p.127-130°C. Accurate mass, calc. for $C_{15}H_{22}NO_4$ (MH^+) 280.1549, obs. 280.1551. ^1H n.m.r. (D_2O) 7.26 (m 5H aromatic) 4.52 (s 2H CH_2Ph) 4.21 (m H-1) 3.41 (t J=9.3 H-8) 3.34 (td J=4.9, 10.0 H-6) 3.22 (t J=9.1 H-7) 3.13 (dd J=4.9, 10.8 H-5) 2.87 (m H-3) 2.14 (m H-2) 2.01 (q J=9.0 H-3′) 1.81 (m 2H H-5′, H-8a) 1.51 (m H-2′). ^{13}C n.m.r. (D_2O) 139.9, 131.3, 131.0 aromatic; 80.7 C-6; 80.5 C-7; 73.5 CH_2Ph; 73.8 C-8a; 72.1 C-1; 71.5 C-8; 55.6 C-5; 54.1 C-3; 35.2 C-2.

Australine (53). A solution of (55) (2.8 g, 6.9 mmol) in ethanol (100 ml) was acidified to pH 1 with hydrochloric acid and stirred with Pearlmann's catalyst (0.23 g) under hydrogen (1 atm). After hydrogen uptake had ceased, the mixture was filtered and the filtrate was adjusted to pH 10 with aqueous ammonia and stirred at room temperature overnight. The solvents were removed under reduced pressure and the residue chromatographed using dichloromethane-methanol-ammonium hydroxide (5:4:1) as eluant, affording a material that possessed an ^1H n.m.r. spectrum that was in agreement with that reported for australine. Crystallisation from methanolic hydrogen chloride gave the title compound as its hydrochloride. M.p. 155-157°C. Accurate mass, calc. for $C_8H_{16}NO_4$ (MH^+) 190.1079, obs. 190.1080. $[\alpha]_D$ + 23.2° (c=1, H_2O). ^1H n.m.r. (D_2O) 4.54 (m H-7) 4.34 (t J=7.3 H-1 or H-2) 4.01 (dd J=7.8, 10.5 H-1 or H-2) 3.86 (dd J=3.1, 13.2 H-8) 3.79 - 3.63 (m 3H H-3, H-5, H-8′) 3.30-3.20 (m 2H H-5′, H-7a) 2.22-2.02 (m 2H H-6, H-6′). ^{13}C n.m.r. (D_2O) 78.1, 75.3, 74.2, 73.3, 70.8 C-1, C-2, C-3, C-7, C-7a; 58.5, 54.9 C-5, C-8; 37.1 C-6.

6-*O*-Methylcastanospermine (59). A solution of mesylate (26) (2.5 g, 6.3 mmol) in tetrahydrofuran (10 ml) was diluted with methanol (90 ml) and then sodium methoxide in methanol (1% sodium, 1 ml) was added. The solution was stirred overnight at room temperature and then held at 80°C for 2 hr. Concentration under reduced pressure and chromatography using dichloromethane-methanol (4:1) as eluent gave the title compound (59) (1.0 g, 4.9 mmol, 78%). Accurate mass, calc. for $C_9H_{18}NO_4$ (MH^+) 204.1236, obs. 204.1234. ^1H n.m.r. (D_2O) 4.31 (m H-1) 3.51 (t J=9 H-8) 3.38 (s 3H OCH_3) 3.34-3.19 (m 3H H-5, H-6, H-7) 2.99 (m H-3) 2.08-2.26 (m 2H H-2, H-3′) 1.93-1.66 (m 2H H-5′, H-8a) 1.62 (m H-2′). ^{13}C n.m.r. (D_2O) 82.4, 80.4 C-6, C-7; 73.9 C-8a; 72.2 C-1; 71.6 C-8; 60.3 -OCH_3; 55.0 C-5; 54.3 C-3; 35.4 C-2.

6-Alkyl or arylamino-6-deoxycastanospermine and 8-alkyl or arylamino-8-deoxyaustraline:- General Method. A solution of mesylate (26) (2.5 g 6.3 mmol) in tetrahydrofuran (10 ml) was diluted with methanol (90 ml) and then sodium methoxide in methanol (1% sodium, 1 ml) was added. Deacetylation of (26) was monitored by t.l.c. (dichloromethane-methanol (9:1)). When (26) had been almost completely converted to the more polar trihydroxymesylate (58), amine (10-20 ml) was added and the solution stirred at 50-80°C overnight. After cooling, the reaction mixture was run through a column of anion exchange resin (Amberlyst A-26, OH form) which was then eluted with water. Fractions containing the products were combined and the solvents and amine were evaporated under reduced pressure. Repeated column chromatography using dichloromethane-methanol-ammonium hydroxide (aqueous, 25% NH_3) (5:4:1) as eluent gave castanospermine and australine amines, together with minor amounts of 6-*O*-methylcastanospermine (59) and of 7-alkylamino-7-deoxy-6,7-di-epi-castanospermine (76).

6-Deoxy-6-methylaminocastanospermine (60). A methanolic solution of methylamine was used in place of the amine in the General Method. This solution was prepared by passing a solution of methylamine hydrochloride (6.5 g, 96 mmol) in methanol (600 ml) through a column of anion exchange resin (Amberlyst A-26) in the free base form. (60) (0.80 g, 3.9 mmol, 63%). Accurate mass, calc. for $C_9H_{19}N_2O_3$ (MH^+) 203.1396, obs. 203.1405. ^1H n.m.r. (D_2O) 4.50 (m H-1) 3.72 (t J=9.2 H-8) 3.61 (t J=9.4 H-7) 3.52 (dd J=4.6, 10.9 H-5) 3.23 (m 2H H-3, H-6) 2.84 (s 3H CH_3) 2.44-2.30 (m 3H H-2, H-3′, H-5′) 2.16 (dd J=42, 9.6 H-8a) 1.80 (m H-2′). ^{13}C n.m.r. (D_2O) 77.2 C-7; 73.5 C-8a; 72.1 C-1; 72.0 C-8; 61.6 C-6; 54.2 C-3; 52.1 C-5; 35.3 C-2; 33.5 CH_3.

6-Allylamino-6-deoxycastanospermine (61). (0.70 g, 3.2 mmol, 48%). Accurate mass, calc. for $C_{11}H_{21}N_2O_3$ (MH^+) 229.1522, obs. 229.1547. ^1H n.m.r. (D_2O) 5.84 (=CH) 5.15 (m 2H =CH_2). 4.35 (m H-1) 3.55 (t J=9.4 H-8) 3.41-3.11 (m 4H H-5, H-7, CH_2N) 3.02 (m, H-3) 2.66 (td J=4.4, 10.1 H-6) 2.26 (m H-2) 2.14 (q J=9.0 H-3′) 1.92 (dd J=4.4, 9.8 H-8a) 1.84 (t J=10.9 H-5′) 1.64 (m H-2′). ^{13}C n.m.r. (D_2O) 137.8 =CH; 119.9 =CH_2; 80.1 C-7; 74.1 C-8a; 72.4, 72.3 C-1, C-8; 60.6 C-6; 55.7, 54.4, 51.5 C-3, C-5, CH_2N; 35.3 C-2.

8-Allylamino-8-deoxyaustraline (62). (0.30 g, 1.3 mmol, 20%). Accurate mass, calc. for $C_{11}H_{21}N_2O_3$ (MH^+) 229.1522, obs. 229.1563. ^1H n.m.r. (D_2O) 5.92 (=CH) 5.20 (m 2H = CH_2) 4.36 (m H-7) 4.21 (t J=8.0 H-1) 3.85 (td J=3.7, 8.5 H-2) 3.24 (m 2H CH_2N), 3.18 (dd J=4.4, 7.6 H-7a) 3.11 (m H-5) 2.84-2.67 (m 4H H-3, H-5′, H-8, H-8′) 2.08-1.87 (m 2H H-6, H-6′). ^{13}C n.m.r. (D_2O) 138.0 =CH; 119.6 =CH_2; 84.1 C-2; 75.6 C-1; 73.4 C-7a; 72.1 C-7; 71.0 C-3; 54.5, 54.3, 54.1 C-5, C-8, CH_2N; 37.9 C-6.

6-Butylamino-6-deoxycastanospermine (63). (0.65 g, 2.7 mmol, 39%). Accurate mass, calc. for $C_{12}H_{25}N_2O_3$ (MH^+) 245.1865, obs 245.1870. ^1H n.m.r. (D_2O) 4.40 (m H-1) 3.60 (t J=9.4 H-8) 3.26 (m 2H H-6, H-7) 3.07 (m, H-3) 2.71 (m 2H H-5, H-CHN) 2.60 (m, H-CHN) 2.32 (m H-2) 2.18 (q J=8.7 H-3′) 1.96 (m 2H H-5′, H-8a) 1.69 (m H-2′) 1.48, 1.34 (m 2H each, CH_2) 0.89 (t 3H J=7.3 CH_3). ^{13}C n.m.r. (D_2O) 79.8 C-7; 74.0 C-8a; 72.3, 72.2 C-1, C-8; 60.8 C-6; 55.4, 54.3 C-3, C-5; 48.7 CH_2N; 35.2, 33.1 C-2, CH_2; 22.2 CH_2; 15.7 CH_3.

8-Butylamino-8-deoxyaustraline (64). (0.76 g, 3.1 mmol, 46%). Accurate mass, calc. for $C_{12}H_{25}N_2O_3$; (MH^+) 245.1865, obs. 245.1863. ^1H n.m.r. (D_2O) 4.43 (m H-7) 4.28 (t J=8.0 H-1) 3.93 (t J=8.3 H-2) 3.26 (dd J=4.5, 7.5 H-7a) 3.17 (m H-5) 2.84 (m 4H H-3, H-5′, H-8, H-8″) 2.69 (m 2H CH_2N) 2.14-1.96 (m 2H H-6, H-6′) 1.54 (m 2H CH_2) 1.40 (m 2H CH_2) 0.98 (m 3H CH_3). ^{13}C n.m.r. (D_2O) 84.5 C-2; 75.9 C-1; 73.7 C-7a; 72.4 C-7; 71.0 C-3; 55.1 C-8; 54.7 C-5; 51.7 CH_2N; 38.0 C-6; 33.4 CH_2; 22.7 CH_2; 16.1 CH_3.

6-Deoxy-6-(2-methylpropylamino)castanospermine (65). (0.48 g, 2.0 mmol, 31%). Accurate mass, calc. for $C_{12}H_{25}N_2O_3$ (MH^+) 245.1865, obs. 245.1866. ^1H n.m.r. (D_2O) 4.34 (m H-1) 3.54 (t J=9.4 H-8) 3.18 (m 2H H-5, H-7) 3.00 (m H-3) 2.56 (td J=4.3, 10.2 H-6) 2.41 (dd J=7.0, 11.6 H-CHN) 2.31-2.20 (m 2H H-2, H-CHN) 2.12 (q J=9.0 H-3′) 1.84 (dd J=9.9, 4.3 H-8a) 1.82 (t J=10.9 H-5′) 1.73-1.56 (m 2H H-2′, CH) 0.82 (m 6H CH_3). ^{13}C n.m.r. (D_2O) 80.0 C-7; 74.1 C-8a; 72.3; 72.2 C-1, C-8; 60.8 C-6; 56.9, 55.7, 54.3 C-3, C-5, CH_2N; 35.1 C-2; 29.6 CH; 22.2 CH_3.

8-Deoxy-8-(2-methylpropylamino)australine (66). (0.48 g, 1.95 mmol, 31%). Accurate mass, calc. for $C_{12}H_{25}N_2O_3$ (MH^+) 245.1865, obs. 245.1861. ^1H n.m.r. (D_2O) 4.32 (m H-7) 4.16 (t J=7.8 H-1) 3.81 (quin J=4.2, 8.4 H-2) 3.14 (dd J=4.4, 7.5 H-7a) 3.06 (m H-5) 2.76-2.63 (m 4H H-3, H-5′, H-8, H-8′) 2.40 (m 2H CH_2N) 2.03-1.86 (m 2H H-6, H-6′) 1.75 (m CH) 0.85 (m 6H CH_3). ^{13}C n.m.r. (D_2O) 84.4 C-2; 75.6 C-1;

73.4 C-7a; 72.1 C-7; 70.4 C-3; 59.6 CH_2N; 55.1, 54.4 C-5, C-8; 37.9 C-6; 29.7 CH; 22.4 CH_3.

6-Deoxy-6-(1-methylpropylamino)castanospermine (67). (0.50 g, 2.0 mmol, 32%). M.p. 156-158°C. Accurate mass, calc. for $C_{12}H_{25}N_2O_3$ (MH^+) 245.1865, obs. 245.1872. ^1H n.m.r. (D_2O) 4.38 (m H-1) 3.58 (t J=9.4 H-8) 3.20 (m 2H H-5, H-7) 3.04 (m, H-3) 2.76-2.61 (m 2H H-6, CHN) 2.30 (m H-2) 2.22 (q J=9.0 H-3′) 1.94 (dd J=9.9, 4.3 H-8a) 1.87 (td J=4.3, 10.9 H-5′) 1.66 (m H-2′) 1.46, 1.32 (m CH_2) 1.01, 0.84 (m 3H each CH_3). ^{13}C n.m.r. 80.7 and 80.5 C-7; 74.3 C-8a; 72.6 and 72.5 C-8; 72.5 C-1; 58.8 and 58.3 C-6; 57.7 and 56.7 C-5; 54.6 and 54.5 CHN; 54.5 C-3; 35.4 C-2; 32.2 and 30.1 CH_2; 22.3 and 20.7, 12.3 and 11.3 CH_3.

8-Deoxy-8-(1-methylpropylamino)australine (68). (0.25 g, 1.0 mmol, 16%). Accurate mass, calc. for $C_{12}H_{25}N_2O_3$ (MH^+) 245.1865, obs. 245.1874. ^1H n.m.r. (D_2O) 4.32 (m H-7) 4.17 (t J=7.8 H-1) 3.80 (td J=3.0, 8.3 H-2) 3.14 (quin J=3.9, 7.6 H-7a) 3.06 (m H-5) 2.71-2.56 (m 5H H-3, H-5′, H-8, H-8′, CHN) 2.04-1.82 (m 2H H-6, H-6′) 1.45, 1.33 (m CH_2) 0.98, 0.84 (m 3H each, CH_3). ^{13}C n.m.r. (D_2O) 84.6 and 84.3 C-2; 75.6 and 75.5 C-1; 73.4 and 73.3 C-7a; 72.1 and 72.0 C-7; 70.8 and 70.6 C-3; 56.8 CHN; 54.6 and 54.3 C-5; 52.3 C-8, 37.9 and 37.8 C-6; 31.0 and 30.8 CH; 20.6 and 20.4, 12.2 and 12.1 CH_3.

6-Deoxy-6-(1-methylbutylamino)castanospermine (69). (0.22 g, 0.85 mmol, 13%). Accurate mass, calc. for $C_{13}H_{27}N_2O_3$; (MH^+) 259.2022, obs. 259.2026. ^1H n.m.r. (D_2O) 4.39 (m H-1) 3.59 (t J=8.8 H-8) 3.33 (m 2H H-5, H-7) 3.21 (m, H-3) 3.10-2.70 (m 2H H-6, CHN) 2.31 (m H-2) 2.17 (q J=9.0 H-3′) 1.99-1.85 (m 2H H-5′, H-8a) 1.69 (m H-2′) 1.51-1.23 (m 4H $(CH_2)_2$), 1.05, 0.89 (m 3H each CH_3). ^{13}C n.m.r. (D_2O) 80.5 and 80.2 C-7; 74.2 C-8a; 72.6 and 72.5, 72.5 C-1, C-8; 59.1 and 58.2 C-6; 57.1 and 56.5 C-5; 54.5 C-3; 53.6 and 52.8 CHN; 41.6 and 39.9 CH_2; 35.4 C-2; 21.4 and 21.0, 16.2 CH_3.

8-Deoxy-8-(1-methylbutylamino)australine (70). (0.30 g, 1.2 mmol, 19%). Accurate mass, calc. for $C_{13}H_{27}N_2O_3$ (MH^+) 259.2022, obs. 259.2016. ^1H n.m.r. (D_2O) 4.32 (m H-7) 4.16 (t J=7.9 H-1) 3.81 (td J=3.0, 8.5 H-2) 3.14 (quin J=4.2, 8.0 H-7a) 3.05 (m H-5) 2.85-2.49 (m 5H H-3, H-5′, H-8, H-8′, CHN) 2.03-1.82 (m 2H H-6, H-6′) 1.45-1.21 (m 4H (CH_2)) 1.01, 0.86 (m 3H each CH_3). ^{13}C n.m.r. (D_2O) 84.6 and 84.3 C-2; 75.6 and 75.5 C-1; 73.4 and 73.3 C-7a; 72.1 and 72.0 C-7; 70.8 and 70.5 C-3; 55.0 and 54.9 CHN; 54.6 and 54.2 C-5; 52.3 C-8, 40.5 and 40.4 CH_2; 37.9 and 37.8 C-6; 21.2 CH_2; 21.0 and 20.8, 16.1 CH_3.

6-Deoxy-6-(2-methoxyethylamino)castanospermine (71). (0.46 g, 1.9 mmol, 29%). Accurate mass, calc. for $C_{11}H_{23}N_2O_4$ (MH^+) 247.1658, obs. 247.1674. ^1H n.m.r. (D_2O) 4.35 (m H-1) 3.55 (m 3H H-8, CH_2O) 3.31 (s 3H CH_3) 3.19 (m 2H H-5, H-7) 3.00 (m H-3) 2.76 (m 2H CH_2N) 2.61 (td J=4.4, 10.1 H-6) 2.26 (m H-2) 2.14 (q J=9.0 H-3′) 1.93 (dd J=4.4, 9.8 H-8a) 1.86 (t J=10.9 H-5′) 1.66 (m H-2′). ^{13}C n.m.r. (D_2O) 80.0 C-7; 74.0 C-8a; 73.3 CH_2O; 72.2, 72.2 C-1, C-8; 60.7 C-6; 60.5 CH_3; 55.7 C-5; 54.2 C-3; 47.9 CH_2N; 32.1 C-2.

8-Deoxy-8-(2-methoxyethylamino)australine (72). (0.46 g, 1.9 mmol, 29%). Accurate mass, calc. for $C_{11}H_{23}N_2O_4$ (MH^+) 247.1658, obs. 247.1672. ^1H n.m.r. (D_2O) 4.32 (m H-7) 4.16 (t J=7.9 H-1) 3.81 (t J=8.4 H-2) 3.54 (m 2H CH_2O) 3.33 (s 3H CH_3) 3.14 (dd J=4.4, 7.6 H-7a) 3.06 (m H-5) 2.81-2.62 (m 6H H-3, H-5′, H-8, H-8′, CH_2N) 2.18-1.82 (m 2H H-6, H-6′). ^{13}C n.m.r. (D_2O) 84.0 C-2; 75.5 C-1; 73.5 C-7a; 72.8 CH_2O; 72.1 C-7; 70.4 C-3; 60.7 CH_3; 54.4, 54.3 C-5, C-8 or CH_2N; 50.5 C-8 or CH_2N; 37.8 C-6.

8-Benzylamino-8-deoxyaustraline (74). (0.45 g, 1.6 mmol, 26%). M.p. 187-190°C. Accurate mass, calc. for $C_{15}H_{23}N_2O_3$ (MH^+) 279.1709, obs. 279.1723. ^1H n.m.r. (D_2O) 7.36 (m 5H benzyl) 4.31 (m H-7) 4.16 (t J=7.9 H-1) 3.87-3.75 (m 3H H-2, -CH_2Ph) 3.13 (dd J=4.2, 7.6 H-7a) 3.04 (m H-5) 2.78-2.61 (m 4H H-3, H-5′, H-8, H-8′) 2.02-1.86 (m 2H H-6, H-6′). ^{13}C n.m.r. (D_2O) 141.6, 131.5, 131.4, 130.2 aromatic; 84.3 C-2; 75.7 C-1; 73.5 C-8; 72.2 C-7; 70.9 C-3; 55.5 -CH_2Ph; 54.5 C-5; 54.3 C-8; 38.0 C-6.

6-*N*-Benzylacetamido-6-deoxycastanospermine (75). Crude amine (73) (0.64 g, 2.1 mmol), synthesised according to the General Method, was dissolved in pyridine (5 ml) and acetic anhydride (5 ml). The solution was stirred at room temperature overnight, concentrated under reduced pressure and chromatographed on a column using ethyl acetate as eluent. Fractions containing 1,7,8-tri-*O*-acetyl-6-*N*-benzylacetamido-6-deoxycastanospermine were concentrated under reduced pressure and the residue was dissolved in methanol (10 ml). Methanolic sodium methoxide (1% sodium) was added to pH 12 and the solution stirred at room temperature overnight. Concentration under reduced pressure and chromatography using dichloromethane-methanol (5:1) as eluent gave the title amide (75) (0.45 g, 1.5 mmol, 67%).

Accurate mass, calc. for $C_{17}H_{25}N_2O_4$ (MH^+) 321.1814, obs 321.1809. ^1H n.m.r. (D_2O) (500 MHz) 7.55-7.31 (m H aromatic) 5.02 (d J=17, CH_2Ph) 4.81 (bs CH_2Ph) 4.50 (m H-1) 4.44 (d J=16.5 CH_2Ph) 4.14 (td J=4.0, 10.0 H-6) 3.87 (bs H-6) 3.85 (t J=8.7 H-8) 3.82 (t J=8.5 H-7) 3.79 (t J=8.7 H-7) 3.21 (dd J=4.5, 12.0 H-5) 3.13 (m, H-3) 2.43 and 2.25 (s 3H acetate) 2.37 (m H-2) 2.28-2.19 (m 2H H-3′, H-5′) 2.15 (dd J=4.5, 9.5 H-8a) 1.80 (m H-2′). ^{13}C n.m.r. (D_2O) 178.8 and 1.78.1 acetate; 140.0, 139.5, 131.6, 131.3, 130.4, 129.7, 129.0, 128.8 phenyl; 76.0 and 75.5 C-7; 73.7 C-8a; 72.3 and 72.1, 72.0 and 71.7 C-1, C-8; 62.5 C-6; 55.1 and 54.3, 54.2 and 54.0, C-3, C-5; 47.6 CH_2Ph; 35.1 and 35.0 C-2; 24.5 and 24.1 acetate.

1,7,8-Tri-*O*-acetyl-6-amino-6-deoxy-6-*N*,*N*-diethylcastanospermine (78) and 1,2,7-tri-*O*-acetyl-8-amino-8-deoxy-8-*N*,*N*-diethylaustraline (79). Trifluoromethanesulfonic anhydride (0.21 ml) was added to a stirred solution of 1,7,8-tri-*O*-acetylcastanospermine (13) (0.16 g) in dry dichloromethane (5 ml) containing 4-methyl-2,6-di-^{tert}butylpyridine (0.32 g). After 0.5 hours, diethylamine (2 ml) was added and the solution was stirred at room temperature for a further 0.5 hours, then washed with water, dried and evaporated. Chromatography of the residue (EtOAc/Petroleum ether 1:1) afforded the castanospermine derivative (78) (0.020 g). ^1H n.m.r. ($CDCl_3$) : 5.35 (1H, m, H-1), 5.19 (1H, t, J = 9.4 Hz, H-8), 5.00 (1H, t, J = 9.6 Hz, H-7), 3.26 - 3.15 (2H, m, H-3,5), 3.03 (1H, dt, $J_{5e,6}$ = 4.1 Hz, $J_{5a,6}$ = $J_{6,7}$ = 10.7 Hz, H-6), 2.60 (2H, m), 2.45 - 2.24 (3H, m), 2.17 (2H, m, H-3′, 8a), 2.09 - 2.00 (1H, m, H-5′), 2.05, 2.03 and 1.97 (9H, s, OAc), 1.85 (1H, m, H-2′), 0.97 (6H, t, 2 x CH_3). ^{13}C n.m.r. : δ 170.7, 170.6, 169.8 (C = O), 73.3, 71.3, 69.5, 69.0 and 59.5 (CH), 52.6, 50.4, 43.9 and 31.6 (CH_2), 21.1, 21.06 and 14.7 (CH_3). HRMS: MH^+ calc. for $C_{18}H_{31}N_2O_6$: 371.2182; obs. 371.2180.

Further elution ($CHCl_3$/EtOAc/MeOH 5:2:1) gave the australine derivative (79) (0.12 g). ^1H n.m.r. ($CDCl_3$) : δ 5.38 (1H, t, H-2), 5.25 (2H, m, H-1,7), 3.54 (1H, dd, H-7a), 3.21 (1H, m, H-5), 2.98 (1H, dd, H-3), 2.77 (1H, m, H-5′), 2.55 - 2.43 (6H, m, CH_2N), 2.13 - 2.02 (2H, m, H-6,6′), 2.12, 2.05, 2.03 (9H, s, 3 x OAc), 0.98 (6H, t, 2 x CH_3). ^{13}C n.m.r.: δ 170.7, 170.1 and 170.0 (C = 0), 80.3 (C-2), 74.4 and 73.6 (C-1,7), 69.5 (C-7a), 66.6 (C-3), 57.5 (C-8) 52.5 (C-5) 47.5 (NCH_2), 33.7 (C-6), 21.2, 21.1 and 20.1 (CH_3), 11.7 (CH_3). HRMS: MH^+calc. for $C_{18}H_{31}N_2O_6$: 371.2182; obs. 371.2188.

6-*O*-Benzoyl-1,8-*O*-isopropylidenecastanospermine (81). 2,2-Dimethoxypropane (40 ml) was added to a solution of 6-*O*-benzoylcastanospermine (5.0 g) and camphorsulfonic acid (4.55 g, 1.15 eq) in dry *N*,*N*-dimethylformamide (40 ml), and the solution was heated at 70 - 80°C for 1 hour. After cooling, dichloromethane was added and the solution was washed with 5% aqueous sodium carbonate, dried, and concentrated. The residual solvents were removed under high vacuum at 50°C. Trituration of the solid residue with ethyl acetate - hexanes gave title compound (81) (4.03 g, 71%). Recrystallised from ethyl acetate - hexanes it had m.p. 184-185°C (Lit.[36] m.p. 183-184°C). The ^1H n.m.r. spectrum correlated with that reported[36].

6-*O*-Benzoyl-1,8-*O*-cyclohexylidenecastanospermine (82). A solution of 6-*O*-benzoylcastanospermine (25 g) and camphorsulfonic acid (25 g, 1.26 eq) in dry *N*,*N*-dimethylformamide (120 ml), cyclohexanone (160 ml), and triethylorthoformate (80 ml) was heated at 80°C for 1 hour. After cooling the solution was partitioned between dichloromethane and 5% aqueous sodium carbonate. The organic phase was dried, concentrated, and the high boiling material removed at 50°C under high vacuum. The solid residue was stirred with hexanes and then filtered, affording 23.4 g (74%) of title compound (82). Recrystallised from ethyl acetate - hexanes it had m.p. 205-206°C ^1H n.m.r. ($CDCl_3$) δ 8.05, and 7.59-7.41 (5H, aromatics), 5.23 (1H, m, H-6), 4.53 (1H, t, H-1), 3.89-3.79 (2H, m, H-7,8), 3.41 (1H, dd) 3.17-2.88 (4H, m), 2.31-2.17 (1H, m, H-2), 1.97 (1H, dd, H-2′), 1.80-1.28 (10H, m). ^{13}C n.m.r. ($CDCl_3$) δ 166.2 (C=O), 133.2, 129.8, 128.4 (CH), 101.3 (O-C-O), 74.3, 71.5, 70.7, 65.9, 62.6 (CH), 49.3, 49.2, 37.2, 34.4, 32.9, 25.2, 23.2, 23.0 (CH_2). HRMS: MH^+ calc. for $C_{21}H_{28}NO_5$ requires 374.1967, obs. 374.1961.

1,8-*O*-Isopropylidene-6-*O*-methanesulfonyl-7-*O*-methoxymethylcastanospermine (80). A suspension of 6-*O*-benzoyl-1,8-*O*-isopropylidenecastanospermine (81) (3.5 g) in dry toluene (80 ml) containing diisopropylethylamine (6.2 ml, 3 eq) and bromomethyl methyl ether (1.46 ml. 1.5 eq) was heated with stirring at 80°C for 1 hour. The cooled solution was then washed with water (x2), dried and concentrated to dryness. The residue was dissolved in methanol (75 ml) and the solution was adjusted to pH 11 with aq sodium hydroxide. After standing at room temperature overnight the solution was concentrated *in*

vacuo and the residue was partitioned between dichloromethane and water. The water was back extracted with dichloromethane and the combined organic extracts were processed normally. This crude product was then dissolved in pyridine (25 ml) and treated with methanesulfonyl chloride (1.85 ml, 2 eq). After 1 hour the solution was diluted with dichloromethane and washed with water (x2). Conventional processing followed by flash chromatography (ethyl acetate/hexanes 3:1) gave the 6-mesylate (80) (1.93 g, 46% overall). ^{1}H n.m.r. ($CDCl_3$) δ 4.90, 4.73 (2H, d, OCH_2O), 4.60 (1H, m), 4.49 (1H, t), 3.73 (2H, m), 3.42 (3H, s, OCH_3, and 1H, m). 3.10 (3H, s, SO_2CH_3), 3.03-2.85 (2H, m), 2.81 (1H, m), 2.3 - 2.1 (1H, m), 1.85 (1H, m), 1.39 and 1.35 (2 x 3H, s,$(CH_3)_2C$). ^{13}C n.m.r. ($CDCl_3$) δ 101.2, 96.9, 78.0, 77.5, 71.1, 66.9, 63.1, 56.0, 51.3, 49.2, 38.1, 33.1, 27.6, and 24.9. HRMS: MH^+ calc. for $C_{14}H_{25}NO_7S$ requires 352.1430, obs. 352.1427.

1,8-*O*-Cyclohexylidene-7-*O*-methoxymethylcastanospermine (84). A suspension of 6-*O*-benzoyl-1,8-*O*-cyclohexylidenecastanospermine (82) (4.0 g) in toluene (150 ml) was treated with diisopropylethylamine (5.6 ml, 3 eq) and bromomethyl methyl ether (1.31 ml, 1.5 eq) and then heated with stirring at 90°C for 1 hour. The solution was cooled, washed with water (x2), dried, and concentrated to a syrup. This was dissolved in methanol (100 ml) and the solution was adjusted to pH 11 with aq sodium hydroxide and then stored at room temperature overnight. Most of the methanol was removed *in vacuo* and the residue was partitioned between dichloromethane and water. The aqueous phase was back extracted with dichloromethane and the combined organic phases were dried and concentrated to a syrup. Flash chromatography ($CHCl_3$/EtOAc/MeOH 5:2:1) afforded the title alcohol (84) (3.2 g, 92%). ^{1}H n.m.r. ($CDCl_3$): δ4.88 and 4.79 (2H, d, OCH_2O), 4.49 (1H, m, H-1), 3.80 (1H, m, H-6), 3.75 (1H, t, H-7 or H-8), 3.46 (3H, s, OCH_3), 3.41 (1H, t, H-7 or H-8), 3.28 (1H, dd), 2.98 (2H, m), 2.78 (2H, m), 2.29-2.16 (1H, m, H-2), 1.95-1.87 (1H, m, H-2′), 1.77-1.33 (10H, m). ^{13}C n.m.r.: δ 101.1 (O-C-O), 97.5 (CH_2), 84.5, 70.6, 67.9, 65.4 and 63.8 (CH), 55.9 (CH_3), 52.2, 49.3, 36.9, 34.5, 33.1, 25.3, 23.2 and 23.1 (CH_2). HRMS: MH^+ calc. for $C_{16}H_{28}NO_5$ requires 314.1967; obs. 314.1970.

1,8-*O*-Cyclohexylidene-6-*O*-methanesulfonyl-7-*O*-methoxymethylcastanospermine (85). 6-*O*-Benzoyl-1,8-*O*-cyclohexylidenecastanospermine (71) (8.2 g) was converted into 1,8-*O*-cyclohexylidene-7-*O*-methoxymethylcastanospermine (73) as outlined above. The crude product of alcohol (73) was dissolved in dry dichloromethane (60 ml) containing triethylamine (9.2 ml, 3 eq). Methanesulfonyl chloride (3.4 ml, 2 eq) was added with cooling (ice bath) and the solution was stirred at room temperature for 1 hour - and then washed with water, dried and concentrated to a white solid. Trituration with hexanes gave 7.07 g (82%) of title compound (85). Recrystallised from ethyl acetate - hexanes it had m.p. 143-145°C. ^{1}H n.m.r. ($CDCl_3$): δ 4.96 and 4.75 (2H, pr d), 4.66 - 4.60 (1H, m), 4.51 (1H, t), 3.80 - 3.72 (2H, m), 3.47 - 3.39 (2H, m), 3.44 (3H, s), 3.11 (3H, s), 3.04 - 2.96 (2H,m), 2.87 - 2.80 (1H, m), 2.27 - 2.17 (1H, m), 2.05 - 1.89 (1H, m), 1.68 - 1.31 (10H, m). ^{13}C n.m.r. δ 101.4 (C), 97.0 (CH_2), 77.7, 77.3, 70.6, 66.8, 63.3 (CH), 56.1 (CH_3), 51.3, 49.3 (CH_2), 38.2 (CH_3), 36.8, 34.6, 33.2, 25.4, 23.1 (CH_2). HRMS: MH^+ calc. for $C_{17}H_{30}NO_7S$: 392.1743; obs. 392.1747.

6-Azido-1,8-*O*-cyclohexylidene-6-deoxy-7-*O*-methoxymethylcastanospermine (87). 6-*O*-Benzoyl-1,8-*O*-cyclohexylidenecastanospermine (82) (4.5 g) was converted into the mesylate (85) as outlined above. The crude product was dissolved in dimethylsulfoxide (50 ml), sodium azide (3.9 g) was added and the mixture was heated with stirring at 90°C for 2.5 hours. The cooled solution was diluted with chloroform, washed with water (x2), dried and concentrated. Flash chromatography (EtOAc/hexanes 2:3) of the residue afforded title azide (2.70 g, 66%). ^{1}H n.m.r. ($CDCl_3$): δ 5.03 and 4.75 (2H, d, OCH_2O), 4.50 (1H, t, H-1), 3.77, (1H, t, H-8), 3.60 (2H, m, H-6,7), 3.49 (3H, s, OCH_3), 3.23 (1H, dd, H-5), 3.04 - 2.90 (2H, m), 2.80 - 2.67 (2H, m), 2.25 - 2.15 (1H, m, H-2), 1.98 - 1.88 (1H, m, H-2′), 1.70 - 1.35 (10H, m). ^{13}C n.m.r. δ 101.1 (C), 96.8 (CH_2), 78.8, 70.5, 66.6, 63.6, 59.3 (CH), 55.9 (CH_3), 50.8, 48.8, 36.7, 34.6, 33.0, 25.2, and 23.0 (CH_2). HRMS: MH^+ calc. for $C_{16}H_{27}NO_4$: 339.2032; Obs. 339.2020.

6-Azido-6-deoxy-1,8-*O*-isopropylidene-7-*O*-methoxymethylcastanospermine (86). The crude product from the preparation of 1,8-*O*-isopropylidene-6-*O*-methanesulfonyl-7-*O*-methoxymethylcastanospermine (80) from 2.5 g of 6-*O*-benzoyl-1,8-*O*-isopropylidenecastanospermine (81) in dimethylsulfoxide (50 ml) was treated with sodium azide (2.5 g) and the mixture was stirred at 80°C for 8 hours. The cooled solution was diluted with chloroform, washed with water (x2), dried and concentrated to a syrup. Flash

chromatography (EtOAc/hexanes ether 2:1) afforded title azide (0.86 g, 38% overall). ^{1}H n.m.r. ($CDCl_3$): δ 4.97, 4.74 (2H, d, OCH_2O), 4.49 (1H, t, H-1), 3.74 (1H, t, H-8), 3.64 - 3.55 (2H, m, H-6,7), 3.47 (3H, s, OCH_3), 3.23 (1H, dd, H-5), 3.03 - 2.86 (2H, m, H-3,9), 2.78 - 2.68 (2H, m, H-3′, 5′), 2.28 - 2.15 (1H, m, H-2), 1.94 - 1.87 (1H, m, H-2′), 1.38, 1.35 (6H, s, $C(CH_3)_2$). ^{13}C n.m.r.: δ 101.2 (OCO), 96.9 (OCH_2O), 79.1 (C-7), 71.2 (C-1), 70.0 (C-8), 63.7 (C-8a), 59.8 (C-6), 56.0 (OCH_3), 51.0 (C-5), 49.0 (C-3), 33.2 (C-2), 27.8, 25.1 ($C(CH_3)_2$). HRMS: MH^+ calc. for $C_{13}H_{23}N_4O_4$: 299.1719; obs. 299.1725.

6-Amino-6-*N*-butyryl-6-deoxycastanospermine (88). A solution of 6-azido-6-deoxy-1,8-*O*-isopropylidene-7-*O*-methoxymethylcastanospermine (86) (0.8 g) in ethyl acetate (30 ml) containing 10% palladium on charcoal (0.1 g) was stirred in an atmosphere of hydrogen for 3 hours. After removal of the catalyst and solvent the residue was dissolved in dichloromethane and treated with triethylamine (0.9 ml) and then butyryl chloride (0.29 ml). After 0.5 hours the solution was washed with water, dried, concentrated, and the residue was dissolved in 50% aqueous trifluoroacetic acid (10 ml) and allowed to stand at room temperature overnight. The solution was diluted with water, concentrated to dryness and then the residue was redissolved in water and eluted down an ion exchange column (Amberlyst A26, OH form). Fractions containing the product were combined and evaporated to give the *N*-butyrate (88) (0.41 g, 45%). Recrystallised from methanol/ether it had m.p. 212-213°C, ^{1}H n.m.r. (d_6 DMSO) : 4.12 (1H, t, H-1), 3.66 (1H, dt, H-6), 3.42 (1H, t, H-8), 3.13 (1H, t, H-7), 2.95 (2H, m), 2.14 - 2.03 (3H, m), 1.89 (1H, dd), 1.70 - 1.45 (5H, m), 0.85 (3H, t). ^{13}C n.m.r. : 173.5 (C=O), 77.6, 74.3, 71.2, 70.8 (CH), 56.5, 53.3 (CH_2), 52.6 (CH), 38.9, 35.0, 20.1 (CH_2), 15.1 (CH_3). HRMS: MH^+ calc. for $C_{12}H_{23}N_2O_4$: 259.1658; Obs., 259.1650.

6-Amino-6-*N*-benzoyl-6-deoxycastanospermine (89). A solution of 6-azido-1,8-*O*-cyclohexylidene-6-deoxy-7-*O*-methoxymethylcastanospermine (87) (0.80 g) in ethanol (30 ml) with 10% palladium on charcoal (0.1 g) was stirred in an atmosphere of hydrogen for 4 hours. After removal of the solids and solvent the residue was dissolved in dry dichloromethane (20 ml) and then triethylamine (1.4 ml) and benzoyl chloride (0.6 ml) were added. After 0.5 hours the solution was washed with water, dried, and concentrated. The crude product was dissolved in 30% aqueous trifluoroacetic acid (20 ml) and the solution allowed to stand at room temperature overnight, then diluted with water and extracted twice with dichloromethane. The aqueous phase was evaporated and the residue was stirred in methanol with excess Amberlyst A21 base resin and then applied to a silica gel column. Elution with CH_2Cl_2/MeOH 5:1 afforded the title *N*-benzoate (0.66 g, 67%). ^{1}H n.m.r. (D_2O) : δ 7.88 - 7.59 (5H, m, aromatic), 4.54 (1H, brs), 4.22 (1H, m), 3.82 (1H, t), 3.66 (1H, t), 3.33 - 3.19 (2H, m), 2.42 - 2.15 (4H, m), 1.85 (1H, m). ^{13}C n.m.r.: δ 174.0, 136.2, 134.9, 131.4, 129.8, 79.0, 73.9, 72.4, 72.3, 56.1, 54.2, 35.3. HRMS: MH^+ calc. for $C_{15}H_{21}N_2O_4$: 293.1501; Obs. 293.1505.

6-Amino-6-*N*-benzyl-1,8-*O*-cyclohexylidene-6-deoxy-7-*O*-methoxymethylcastanospermine (90). A solution of 1,8-*O*-cyclohexylidene-6-*O*-methanesulfonyl-7-*O*-methoxymethylcastanospermine (85) (1.0 g) in dimethylsulfoxide (10 ml) containing benzyl amine (1.4 ml) was heated at 90°C for 24 hours. Dichloromethane was added and the solution was washed with water (x2) dried, and concentrated to a syrup. Chromatography ($CHCl_3$/EtOAc/MeOH 10:4:1) gave title compound (90) (0.48 g, 47% yield). ^{1}H n.m.r. ($CDCl_3$) : 7.33 - 7.21 (5H, m, aromatic), 4.96, 4.73 (2H, d, OCH_2O), 4.49, (1H, t, H-1), 3.86, 3.74 (2H, d, $ArCH_2$), 3.78 (1H, t, H-8), 3.53 (1H, t, H-7), 3.38 (3H, s, OCH_3), 3.29 (1H, dd, H-5), 3.02 - 2.89 (3H, m, H-3,6,8a), 2.78 - 2.70 (2H, m, H-3′, 5′), 2.21 (1H, m, H-2), 1.90 (1H, m, H-2′), 1.75 (10H, m), ^{13}C n.m.r. : 140.3, 128.5, 127.9, 127.0 (aromatic), 100.9 (C), 97.3 (CH_2), 88.2, 70.6, 67.0, 64.0 (CH) 56.0 (CH_3), 55.5 (CH), 52.0, 51.8, 49.2, 36.6, 34.6, 33.1, 25.3, 23.0 (CH_2). HRMS: MH^+ calc. for $C_{23}H_{35}N_2O_4$: 403.2597; Obs. 403.2601.

6-Amino-6-*N*-benzyl-6-deoxycastanospermine (73). A solution of 6-amino-6-*N*-benzyl-1,8-*O*-cyclohexylidene-6-deoxy-7-*O*-methoxymethylcastanospermine (90) (0.45 g) in 30% aqueous trifluoroacetic acid (30 ml) was allowed to stand at room temperature for 18 hours. It was then diluted with water and extracted (x2) with dichloromethane. The aqueous phase was concentrated to dryness and then redissolved in water and eluted down an ion exchange column (Amberlyst A26 OH form). The fractions containing product were combined and evaporated affording the 6-*N*-benzyl compound (73) (0.29 g, 93%). ^{1}H n.m.r. (D_2O): δ 7.67 - 7.57 (5H, aromatics), 4.61 (1H, br s, H-1), 4.09 and 3.94 (2H, d, NCH_2Ph), 3.78 (1H, t,

H-8), 3.55-3.46 (2H, m, H-5,7), 3.28 (1H, t, H-3) 2.90 (1H, dt, H-6), 2.53 (1H, m, H-2), 2.41 (1H, dd, H-3′), 2.17 (2H, m, H-5′, 8a), 1.90 (1H, m, H-2′). ^{13}C n.m.r.: δ 141.7, 131.6, 131.4 and 130.3 (aromatics), 80.2 (C-7), 74.3 (C-8a), 72.6, 72.5 (C-1,8), 60.2 (C-6), 55.9 (C-5), 54.5 (C-3), 53.1 (NCH_2Ph), 35.4 (C-2). HRMS: MH^+ calc. for $C_{15}H_{23}N_2O_3$: 279.1709; Obs. 279.1702.

6-Amino-1,8-*O*-cyclohexylidene-6-deoxy-6-*N*-bis(2′-hydroxyethyl)-7-*O*-methoxymethylcastanospermine (91). A solution of 1,8-*O*-cyclohexylidene-6-*O*-methanesulfonyl-7-*O*-methoxymethylcastanospermine (85) (1.2 g) in dimethylsulfoxide (25 ml) containing diethanolamine (5 g) was heated at 90°C for 5 hours. The solution was diluted with chloroform, washed (x2) with water, dried, and evaporated. Chromatography ($CHCl_3$/EtOAc/MeOH 5:2:1) of the residue afforded 0.948 g (77% yield) of title compound (91). ^{1}H n.m.r. ($CDCl_3$) : δ 4.94, 4.79 (2H, d, OCH_2O), 4.44 (1H, dt, H-1), 3.74-3.52 (6H, m), 3.43 (3H, s, OCH_3), 3.15-2.57 (10H, m), 2.24 (1H, m), 1.92 (1H, m), 1.73-1.25 (10H, m). ^{13}C n.m.r. : δ 101.3 (C), 97.9 (CH_2), 79.1, 70.0, 69.0, 64.1 (CH), 60.3 (CH_2), 58.8 (CH), 56.0 (CH_3), 53.0, 49.1, 47.7, 36.2, 34.4, 33.1, 25.3, 23.0 (CH_2). HRMS: MH^+ calc. for $C_{20}H_{37}N_2O_6$: 401.2652; Obs. 401.2650.

6-Amino-6-deoxy-6-*N*-bis(2′-hydroxyethyl)castanospermine (94). A solution of 6-amino-1,8-*O*-cyclohexylidene-6-deoxy-6-*N*-bis(2′-hydroxyethyl)-7-*O*-methoxymethylcastanospermine (91) (0.9 g) in 30% aqueous trifluoroacetic acid (30 ml) was allowed to stand at room temperature for 2 days, and then diluted with water and washed (x2) with dichloromethane. The aqueous layer was concentrated to dryness, the residue redissolved in water, and eluted down a column of Amberlyst A26 resin (OH form). Fractions containing product were combined and evaporated to give title compound (94) (0.55 g, 88%). ^{1}H n.m.r. (D_2O) : δ 4.48 (1H, t, H-1), 3.77-3.63 (5H, m, H-8, $(CH_2OH)_2$), 3.58 (1H, t, H-7) 3.23 (1H, dd, H-5), 3.14 (1H, t, H-3), 2.98-2.89 (2H, m, NCH_2), 2.79-2.72 (3H, m, NCH_2, H-6), (2.38 1H, m, H-2), 2.30-2.15 (2H, m, H-3′, 5′), 2.04 (1H, dd, H-8a), 1.76 (1H, m, H-2′), ^{13}C n.m.r.: δ 76.9, 74.0, 72.9, 72.4, 65.0 (CH), 62.7, 55.0, 54.6, 51.5, 41.5, 35.4 (CH_2). HRMS: MH^+ calc. for $C_{12}H_{25}N_2O_5$: 277.1763; Obs. 277.1767.

6-Amino-6-*N*-butyl-1,8-*O*-cyclohexylidene-6-deoxy-6-*N*-ethyl-7-*O*-methoxymethylcastanospermine (92). A solution of 1,8-*O*-cyclohexylidene-6-*O*-methanesulfonyl-7-*O*-methoxymethylcastanospermine (85) (1.0 g) in dimethylsulfoxide (5 ml) containing *N*-ethyl butylamine (1.75 ml) was heated at 90°C for 10 hours. Then the black solution was diluted with chloroform, washed with water (x2), dried and concentrated. Chromatography (EtOAc) of the residue gave title compound (92) (0.60 g, 59%). ^{1}H n.m.r. ($CDCl_3$) : δ 4.86 (2H, dd, OCH_2O), 4.43 (1H, m, H-1), 3.75 - 3.67 (2H, m, H-7,8), 3.46 (3H, s, OCH_3), 3.06 - 2.96 (3H, m), 2.81 - 2.46 (7H, m), 2.22 (1H, m, H-2), 1.91 (1H, m, H-2′), 1.74 - 1.13 (14H, m), 1.02 (3H, t, CH_3), 0.90 (3H, t, CH_3), ^{13}C n.m.r. : δ 101.1 (C), 97.1 (CH_2), 76.8, 70.2, 68.6, 64.5, 59.3 (CH), 56.0 (CH_3), 50.7, 49.2, 48.8, 44.7, 36.3, 34.6, 33.2, 31.9, 25.4, 23.0, 20.4 (CH_2), 14.9, 14.1 (CH_3). HRMS: MH^+ calc. for $C_{22}H_{41}N_2O_4$: 397.3066; Obs. 397.3065.

6-Amino-6-deoxy-6-*N*,*N*,-diethyl-1,8-*O*-isopropylidene-7-*O*-methoxymethyl castanospermine (93). A solution of 1,8-*O*-isopropylidene-6-*O*-methanesulfonyl-7-*O*-methoxymethylcastanospermine (80) (1.0 g) in dimethylsulfoxide (20 ml) and diethylamine (10 ml) was heated in an oil bath at 100°C under a reflux condenser for 24h. Chloroform was added and the solution was washed with water (x2), dried and concentrated to a syrup. Chromatography (EtOAc/MeOH 7:1) afforded title compound (0.72 g, 77%). ^{1}H n.m.r. ($CDCl_3$) : 4.82 (2H, s, OCH_2O), 4.41 (1H, m, H-1), 3.68 (2H, m, H-7,8), 3.43 (3H, s, OCH_3), 3.07 - 2.95 (3H, m, H-3,5,6), 2.77 - 2.53 (7H, m, H-3′, 5′, 8a, CH_2N), 2.23 (1H, m, H-2), 1.91 (1H, m, H-2′), 1.38 and 1.36 (6H, s, $C(CH_3)_2$), 1.03 (6H, t, CH_3). ^{13}C n.m.r. : δ 101.1 (C), 97.0 (CH_2), 76.8 (C-7), 70.8 (C-1), 68.9 (C-8), 64.5 (C-8a), 59.6 (C-6), 55.7 (OCH_3), 49.4 (C-5), 48.7 (C-3), 44.3 (CH_2N), 33.3 (C-2), 27.3 and 24.9 (CH_3), 14.7 (CH_3). HRMS: MH^+ calc. for $C_{17}H_{33}N_2O_4$ 329.2440; obs. 329.2433.

6-Amino-6-*N*-butyl-6-deoxy-6-*N*-ethylcastanospermine (95). A solution of 6-amino-6-*N*-butyl-1,8-*O*-cyclohexylidene-6-deoxy-6-*N*-ethyl-7-O-methoxymethylcastanospermine (92) (0.56 g) in 30% aqueous trifluoroacetic acid (30 ml) was allowed to stand at room temperature for 2 days. It was then diluted with water, extracted twice with dichloromethane, and the aqueous phase was then concentrated to dryness and eluted in water down an Amberlyst A26 (OH form) column. This material was then chromatographed (CH_2Cl_2/MeOH 6:1) to give title compound (95) (0.20 g, 52%). ^{1}H n.m.r. (D_2O) : δ 4.44 (1H, m, H-1), 3.65 (2H, m, H-7,8), 3.14 (2H, m), 2.98 - 2.54 (5H, m), 2.37 (1H, m, H-2), 2.27 - 2.14 (2H, m, H-3′,5′), 1.99 (1H, dd, H-8a), 1.74 (1H, m, H-2′), 1.58 - 1.44 (2H, m), 1.41 - 1.29 (2H, m), 1.13 (3H, t), 0.95 (3H,

t). ^{13}C n.m.r. : δ 76.5, 73.7, 73.1, 72.2, 62.3 (CH), 54.5, 52.8, 51.8, 47.6, 35.2, 32.2, 22.8 (CH_2), 15.9, 15.0 (CH_3). HRMS: MH^+ calc. for $C_{14}H_{29}N_2O_3$: 273.2178; Obs. 273.2174.

6-Amino-6-deoxy-6-*N*,*N*-diethylcastanospermine (96). A solution of 6-amino-6-deoxy-6-*N*,*N*-diethyl-1,8-*O*-isopropylidene-7-*O*-methoxymethylcastanospermine (93) (0.7 g) in 30% aqueous trifluoroacetic acid was allowed to stand at room temperature for 2 days, and then evaporated to dryness. Elution in water down an ion exchange column (Amberlyst A26, OH form) afforded 0.44 g (95%) of title compound (96). ^1H n.m.r. ($CDCl_3$): 4.41 (1H, brs, H-1), 3.79 (1H, t, H-8), 3.36 (1H, t, H-7), 3.13 (2H, m, H-3,5), 2.81 - 2.63 (3H, m, H-6, NCH_2), 2.43 (2H, m, NCH_2), 2.21 (1H, m, H-2), 2.06 (1H, dd H-5'), 1.94 (1H, t, H-3'), 1.78 (2H, m, H-2', 8a), 1.04 (6H, t, CH_3). ^{13}C n.m.r.: 73.4 (C-7), 72.0 (C-8a), 70.5 (C-8), 69.9 (C-1), 61.5 (C-6), 52.6 (C-5), 48.8 (C-3), 43.5 (NCH_2), 33.2 (C-2), 14.6 (CH_3). HRMS: MH^+ calc. for $C_{12}H_{25}N_2O_3$: 245.1865; Obs. 245.1863.

6-*O*-Butyl-1,8-*O*-cyclohexylidene-7-*O*-methoxymethylcastanospermine (100). A solution of 1,8-*O*-cyclohexylidene-7-*O*-methoxymethylcastanospermine (84)(1.0 g) in dry dimethylsulfoxide (10 ml) was added slowly with stirring to a suspension of potassium hydride (0.25 g, washed free of paraffin oil with dry tetrahydrofuran) in dry dimethylsulfoxide (5 ml) containing n-butyl bromide (1.7 ml, 5 eq) with cooling to keep the reaction temperature ≤ 25°C. The mixture was stirred at room temperature for 3 hours and then quenched by the addition of ethanol and partitioned between chloroform and water. The organic phase was dried and concentrated to a syrup. Flash chromatography (EtOAc) afforded the title n-butyl ether (100) (0.5 g, 42%). ^1H n.m.r. ($CDCl_3$): 4.88, 4.80 (2H, d, OCH_2O), 4.47 (1H, t, H-1), 3.75 - 3.46 (5H, m, H-6,7,8, and OCH_2Pr), 3.44 (3H, s, OCH_3), 3.15 (1H, dd), 3.00 - 2.76 (4H, m), 2.18 and 1.92 (2H, m, H-2,2'), 1.75 - 1.22 (14H, m), 0.91 (3H, t, CH_3). ^{13}C n.m.r.: δ 101.0 (C), 96.6 (CH_2), 79.2, 77.5, (CH), 70.9 (CH_2), 70.6, 66.6, 63.1 (CH), 55.5 (CH_3), 51.1, 50.0, 36.5, 34.6, 33.3, 32.3, 25.5, 23.2, 19.4 (CH_2), 14.1 (CH_3). HRMS: MH^+ Calc for $C_{20}H_{36}NO_5$ requires 370.2593; Obs. 370.2593.

6-*O*-Butylcastanospermine (101). A solution of 6-*O*-butyl-1,8-*O*-cyclohexylidene-7-*O*-methoxymethylcastanospermine (100) (0.5 g) in 30% aqueous trifluoroacetic acid (50 ml) was allowed to stand at room temperature for 5 hours, and then diluted with water (50 ml) and extracted (x2) with dichloromethane. The aqueous phase was concentrated to a syrup which was redissolved in water and eluted down an ion exchange column (Amberlyst A26 OH form) with water. Fractions containing the product were combined and evaporated *in vacuo* to give the n-butyl ether (101) (0.288 g, 86%). ^1H n.m.r. (D_2O): δ 4.33 (1H, t), 3.63 - 3.48 (3H, m), 3.29 (3H, m), 3.00 (1H, t), 2.31 - 2.09 (2H, m), 1.94 - 1.86 (2H, m), 1.68 - 1.57 (1H, m), 1.53 - 1.43 (2H, m), 1.33 - 1.21 (2H, m), 0.82 (3H, t). ^{13}C n.m.r. δ 80.9, 80.4, 73.8 (CH), 73.4 (CH_2), 72.1, 71.6 (CH), 55.6, 54.2, 35.3, 33.8, 21.1 (CH_2), 15.7 (CH_3). HRMS: MH^+ calc. for $C_{12}H_{24}NO_4$: 246.1705; Obs. 246.1713.

1,8-*O*-Cyclohexylidene-6-*epi*-7-*O*-methoxymethyl-6-*C*-vinylcastanospermine (103). Trifluoroacetic anhydride (0.67 ml) was added dropwise to a stirred solution of dimethylsulfoxide (0.57 ml) in dry tetrahydrofuran (40 ml) at -70°C, and then after 15 mins. a solution of 1,8-*O*-cyclohexylidene-7-*O*-methoxymethylcastanospermine (84) (1.0 g) in dry tetrahydrofuran (10 ml) was added slowly maintaining the reaction temperature ≤-60°C. After 20 mins. triethylamine (2-3 ml) was added and the solution was allowed to warm to room temperature by which time t.l.c. examination (CH_2Cl_2/acetone 4:1) showed the alcohol (84) was fully consumed to the less polar ketone (102). The solution was recooled to -70°C and vinyl magnesium bromide (1.0 M in THF) was added slowly until t.l.c. examination of the reaction indicated the ketone (102) was fully consumed. The resulting mixture was partitioned between saturated aqueous ammonium chloride and chloroform, and the organic phase was washed with saturated aqueous sodium bicarbonate and processed normally to give a pale yellow solid (1.24 g). Recrystallisation from petroleum ether afforded 0.57 g of title compound (103) and chromatography of the mother liquors gave another 0.24 g. (total 0.81 g, 74%). Mp 138-139°C. ^1H n.m.r. ($CDCl_3$): 5.84 (1H, dd, CH=C), 5.45 and 5.23 (2H, d, $=CH_2$), 4.96 and 4.63 (2H, d, OCH_2O), 4.51 (1H, m, H-1), 4.23 (1H, t, H-8), 3.69 (1H, d, H-7), 3.50 (1H, m, H-3), 3.36 (3H, s, OCH_3), 2.99 (1H, t, H-8a), 2.91 (2H, dd, H-5,5'), 2.79 (1H, m, H-3'), 2.12 (1H, m, H-2), 1.90 (1H, m, H-2'), 1.76-1.36 (10H, m). ^{13}C n.m.r.: δ 142.0 (CH=), 115.1 ($=CH_2$), 100.8 (OCO), 96.5 (OCH_2O), 78.9 (C-7), 78.0 (C-6), 70.6 (C-1), 64.2 (C-8a), 63.9 (C-8), 56.0 (OCH_3), 55.4 (C-5), 49.4 (C-3), 33.1 (C-2), 36.8, 34.8, 25.3 and 23.0 (CH_2). HRMS MH^+ calc. for $C_{18}H_{30}NO_5$

340.2124; obs. 340.2115.

6-*Epi*-6-*C*-vinylcastanospermine (105). A solution of 1,8-*O*-cyclohexylidene-6-*epi*-7-*O*-methoxymethyl-6-*C*-vinylcastanospermine (103) (0.39 g) in 30% aqueous trifluoroacetic acid (30 ml) was allowed to stand at room temperature overnight. The resulting dark solution was diluted with water, extracted (x2) with dichloromethane and the aqueous phase was concentrated to dryness. The residue was eluted in water from a column of Amberlyst A26 (OH form) resin affording title compound (105) (0.208 g, 84%). ^{1}H n.m.r. (D_2O): 5.83 (1H, dd, CH=), 5.34 and 5.24 (2H, d, $=CH_2$), 4.33 (1H, m, H-1), 3.79 (1H, t, H-8), 3.38 (1H, d, H-7), 3.02 (1H, t, H-3), 2.84 (1H, d, H-5), 2.23 (1H, m, H-2), 2.20 (1H, d, H-5′), 2.11 (1H, dd, H-3′), 1.92 (1H, dd, H-8a), 1.67 (1H, m, H-2′). ^{13}C n.m.r.: 142.4 (CH=), 118.3 ($=CH_2$), 80.1 (C-7), 77.8 (C-6), 74.3 (C-8a), 73.1 (C-1), 70.8 (C-8), 62.1 (C-5), 54.3 (C-3), 35.4 (C-2). HRMS: MH^+ calc. for $C_{10}H_{28}NO_4$ 216.1236; obs. 216.1232.

1,8-*O*-Cyclohexylidene-6-*epi*-7-*O*-methoxymethyl-6-*C*-methylcastanospermine (104). 1,8-*O*-Cyclohexylidene-7-*O*-methoxymethylcastanospermine (84) (1.0 g) was oxidised and treated *in situ* with methyl magnesium chloride (2M in THF) in the same way as described above for the preparation of (103). Chromatography of the crude product gave 0.75 g (72%) of title compound (104). ^{1}H n.m.r. ($CDCl_3$): 5.08 and 4.72 (2H, d, OCH_2O), 4.45 (1H, t, H-1), 4.14 (1H, t, H-8), 3.49 (1H, d, H-7), 3.44 (3H, s, OCH_3), 3.43 (1H, m, H-3), 3.07 (1H, d, H-5), 2.85 (1H, dd, H-8a), 2.74 (1H, d, H-5′), 2.73 (1H, m, H-3′), 2.21-2.04 (1H, m, H-2), 1.93-1.86 (1H, m, H-2′), 1.73-1.26 (10H, m). ^{13}C n.m.r.: 100.9 (C), 97.0 (CH_2), 80.2 (C-7), 74.8 (C-6), 70.4 (C-1), 65.2 (C-8), 64.7 (C-8a), 57.1 (C-5), 56.2 (OCH_3), 49.4 (C-3), 36.6, 34.7 (CH_2), 33.2 (C-2), 25.5 (CH_3), 25.4, 23.0 (CH_2). HRMS: MH^+ calc. for $C_{17}H_{30}NO_5$ 328.2124; obs. 328.2123.

6-*Epi*-6-*C*-methylcastanospermine (106). 1,8-*O*-Cyclohexylidene-6-*epi*-7-*O*-methoxymethyl-6-*C*-methylcastanospermine (104) (0.42 g) was hydrolysed and the product was purified in the same manner as described above for (105), to give 0.24 g (92%) of title compound. ^{1}H n.m.r. (D_2O): 4.22 (1H, t, H-1), 3.63 (1H, t, H-8), 3.10 (1H, d, H-7), 2.93 (1H, dt, H-3), 2.79 (1H, d, H-5), 2.21-2.10 (1H, m, H-2), 2.05-1.96 (2H, m, H-3′, 5′), 1.77 (1H, dd, H-8a), 1.61-1.51 (1H, m, H-2′), 1.07 (3H, s, CH_3). ^{13}C n.m.r.: 81.8 (C-7), 74.9 (C-6), 74.7 (C-8a), 73.3 (C-1), 71.2 (C-8), 63.7 (C-5), 54.5 (C-3), 35.6 (C-2), 25.7 (CH_3). HRMS: MH^+ calc. for $C_9H_{18}NO_4$ 204.1236; obs. 204.1237.

1,8-*O*-Cyclohexylidene-6-deoxy-7-*O*-methoxymethyl-6-*C*-vinylcastanospermine (98). A solution of 1,8-*O*-cyclohexylidene-6-*O*-methanesulfonyl-7-*O*-methoxymethylcastanospermine (85) (1.0 g) in toluene (20 ml) containing tetrabutylammonium iodide (2.0 g) was stirred at 80°C for 18 h, and then a further 1.0 g of tetrabutylammonium iodide was added and the reaction temperature was raised to 100°C for 5h. The cooled reaction mixture was washed with water, dried and concentrated to syrupy crude 1,8-*O*-cyclohexylidene-6-deoxy-6-iodo-7-*O*-methoxymethylcastanospermine (97) (0.75 g). ^{1}H n.m.r. ($CDCl_3$): 5.02 and 4.77 (2H, d, OCH_2O), 4.51 (1H, t, H-1), 4.09 (1H, m, H-6), 3.75 (1H, t, H-7), 3.66 (1H, t, H-8), 3.55 (3H, s, OCH_3), 3.52-3.36 (2H, m, H-5,5′), 3.05 (2H, m. H-3,8a), 2.76 (1H, t, H-3′), 2.27-2.14 (1H, m, H-2), 1.92 (1H, dd, H-2′), 1.68 - 1.18 (10H, m). ^{13}C n.m.r.: 101.2(C), 97.3 (CH_2), 80.7 (C-7), 70.8 (C-1), 68.1 (C-8), 64.0 (C-8a), 57.2 (OCH_3), 57.0 (C-5), 47.7 (C-3), 37.0, 34.8 (CH_2), 33.0 (C-2), 27.4 (C-6), 25.3, 23.1 and 23.0 (CH_2). This material was dissolved in dry THF (10 ml), vinyl magnesium bromide (20 ml, 1.0 M in THF) was added and the resulting solution was heated under reflux in an argon atmosphere for 1 h. The cooled solution was partitioned between saturated aqueous ammonium chloride and chloroform, and the organic layer was washed further with saturated aqueous sodium bicarbonate, dried and concentrated. Chromatography of the crude residue afforded title compound (98) (0.34 g, 41%). ^{1}H n.m.r. ($CDCl_3$): 5.70-5.58 (1H, m, CH=), 5.10 (2H, dd, $=CH_2$), 4.89 and 4.55 (2H, d, OCH_2O), 4.43 (1H, t, H-1), 3.72 (1H, t, H-8), 3.45 (1H, t, H-7), 3.31 (3H, s, OCH_3), 3.03-2.85 (3H, m, H-3, 5, 8a), 2.78 - 2.61 (2H, m, H-3′, 5′), 2.51-2.39 (1H, m, H-6), 2.22-2.09 (1H, m, H-2), 1.97-1.83 (1H, m, H-2′), 1.68 - 1.21 (10 H, m). ^{13}C n.m.r.: 137.5 (CH), 117.0 (CH_2), 100.7 (C), 96.7 (CH_2), 78.3 (C-7), 70.7 (C-1), 67.3 (C-8), 64.2 (C-8a), 55.7 (OCH_3), 52.2 (C-5), 48.4 (C-3), 43.0 (C-6), 36.7, 34.8, 33.1, 25.3, 23.0 (CH_2), HRMS: MH^+ calc. for $C_{18}H_{30}NO_4$ 324.2175; obs. 324.2156.

6-Deoxy-6-*C*-vinylcastanospermine (99). 1,8-*O*-Cyclohexylidene-6-deoxy-7-*O*-methoxymethyl-6-*C*-vinylcastanospermine (98) (0.45 g) was hydrolysed and the product purified in the same manner as described above for (105), to give 0.206 g (74%) of title compound (99). ^{1}H n.m.r.: (D_2O) 5.85 (1H, m, CH=), 5.33 (2H, dd, =CH_2), 4.52 (1H, m, H-1), 3.72 (1H, t, H-8), 3.44 (1H, t, H-7), 3.18 (1H, t, H-3), 3.07 (1H, dd, H-5), 2.48-2.41 (2H, m, H-2,6) 2.38-2.06 (3H, m, H-8a,3′,5′), 1.85-1.74 (1H, m, H-2′). ^{13}C n.m.r.: (D_2O) 139.6 (CH), 120.6 (CH_2), 79.6 (C-7), 74.3 (C-8a), 73.3 (C-8), 72.6 (C-1), 57.3 (C-5), 54.4 (C-3), 49.3 (C-6), 35.3 (C-2). HRMS: MH^+ calc. for $C_{10}H_{18}NO_3$ 200.1287; obs. 200.1285.

6-*O*-Benzoyl-7-*O*-*t*-butyldimethylsilyl-1,8-*O*-cyclohexylidenecastanospermine (108). A solution of benzoate (82) (5 g, 13.4 mmol) t-butyldimethylsilylchloride (3.03 g, 20.1 mmol, 1.5 eq) and imidazole (1.8 g, 26.8 mmol, 2 eq) in *N*,*N*-dimethylformamide (70 ml) was stirred at 55°C for 2 hr and then at 40°C overnight. The solution was partitioned between dichloromethane and saturated aqueous sodium hydrogen carbonate. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Column chromatography (hexanes-ethyl acetate (1:1)) gave the title compound (108) (6.9 g, 14.1 mmol, 100.6%). Accurate mass, calc. for $C_{27}H_{41}NO_5Si$ (MH^+) 488.2832, obs. 488.2832. ^{1}H n.m.r. ($CDCl_3$) 7.94, 7.47, 7.35 (5H in total, benzoate) 5.17 (ddd J=5.4, 7.2, 10.2 H-6) 4.42 (bt J=7.0 H-1) 3.70 (m 2H H-7, H-8) 3.21 (dd J=5.2, 13.7 H-5) 3.00 (m 2H H-3, H-8a) 2.78 (m 2H H-3′, H-5′) 2.13 (m H-2) 1.85 (m H-2′) 1.67-1.23 (m 10H) 0.67, 0.00, -0.13 (s 9H, 3H and 3H TBDMS). ^{13}C n.m.r. ($CDCl_3$) 165.8, 132.9, 130.2, 129.8, 128.3, benzoate; 101.0, cyclohexylidene quat.; 75.3, 72.3, 70.7, 66.6, 63.3, C-1, C-6, C-7, C-8, C-8a; 49.7, 49.4, C-3, C-5; 34.8 C-2; 37.1, 33.1, 25.4; 23.2; 22.9, cyclohexylidene; 25.6, 18.0, -4.17; -4.68; TBDMS.

7-*O*-*t*-Butyldimethylsilyl-1,8-*O*-cyclohexylidenecastanospermine (109) and 6-*O*-*t*-butyldimethylsilyl-1,8-*O*-cyclohexylidenecastanospermine (110). A solution of benzoate (108) (6.9 g, 14.1 mmol) in tetrahydrofuran (15 ml) was diluted with methanol (45 ml), and adjusted to pH ~9 with sodium methoxide in methanol (1% sodium) and refluxed overnight when t.l.c. showed the reaction to be complete. The solution was concentrated under reduced pressure and chromatographed (hexanes-ethyl acetate (1:1)) to give first the 7-hydroxy compound (110) (2.0 g, 5.2 mmol, 37%) and then the 6-hydroxy compound (109) (2.5 g, 6.5 mmol, 47%). (109): Accurate mass, calc. for $C_{20}H_{38}NO_4Si$ (MH^+) 384.2570, obs. 384.2557. ^{1}H n.m.r. ($CDCl_3$) 4.35 (t J=6.9 H-1) 3.61 (ddd J=4.9, 7.5, 10.2 H-6) 3.49 (t J=9.9 H-8) 3.31 (dd J=7.6, 9.6 H-7) 3.06 (dd J=4.9, 13.7 H-5) 2.87 (m 2H H-3, H-8a) 2.71 (m 2H H-3′, H-5′) 2.10 (m H-2) 1.78 (m H-2′) 1.49 - 1.21 (m 11H cyclohexyl, -OH) 0.77, 0.00 (s 9H and 6H TBDMS). ^{13}C n.m.r. ($CDCl_3$) 100.9, cyclohexylidene quat.; 78.5 C-7; 70.6 C-1; 69.8 C-6; 66.0 C-8; 63.4 C-8a; 51.4 C-5; 49.4 C-3; 34.8 C-2; 37.1, 32.9, 25.3; 23.1; 22.9, cyclohexylidene; 25.9, 18.3, -4.0; -4.8; TBDMS. (110): Accurate mass, calc. for $C_{20}H_{38}NO_4Si$ (MH^+) 384.2570, obs. 384.2559. ^{1}H n.m.r. ($CDCl_3$) 4.37 (m H-1) 3.65 (ddd J=5.3, 8.1, 10.3 H-6) 3.56 (t J=10.1 H-8) 3.34 (dd J=8.1, 10.1 H-7) 2.95 (dd J=5.3, 13.9 H-5) 2.87 (m 2H H-3, H-8a) 2.66 (m 2H H-3′, H-5′) 2.10 (m H-2) 1.81 (m H-2′) 1.67-1.11 (m 11H cyclohexyl, -OH) 0.78, 0.02 (s 9H and 6H TBDMS). ^{13}C n.m.r. ($CDCl_3$) 101.1 cyclohexylidene quat.; 77.1 C-7; 70.7 C-1; 70.1 C-6; 65.6 C-8; 63.1 C-8a; 53.1 C-5; 49.2 C-3; 34.6 C-2; 37.2, 32.9, 25.3; 23.2; 23.1, cyclohexylidene; 25.3, 18.1, -4.5; -4.6; TBDMS.

7-*O*-*t*-Butyldimethylsilyl-1,8-*O*-cyclohexylidene-6-*epi*castanospermine (111). A stirred solution of dimethylsulphoxide (0.81 ml, 0.89 g, 2.2 eq) in dry dichloromethane (10 ml) was cooled in a dry ice-acetone bath. A solution of oxalyl chloride in dichloromethane (2M, 5.0 ml, 10 mmol, 1.9 eq) was added followed, at 20 min intervals, by a solution of alcohol (109) (2.0 g, 5.2 mmol) in dichloromethane (20 ml) and triethylamine (5 ml, excess). The reaction mixture was warmed to 0°C, diluted with ethanol (2 vol) and re-cooled to -30°C whereupon sodium borohydride (1.0 g) was added. After warming slowly to room temperature the solution was concentrated to half its original volume under reduced pressure and then partitioned between dichloromethane and water. The organic phase was dried ($MgSO_4$), concentrated under reduced pressure and subjected to chromatography [dichloromethane - methanol (15:1 - 9.1)] to give the less polar inverted alcohol (111) (1.2 g, 3.1 mmol, 60%) and starting material (0.58 g, 1.5 mmol, 29%). (111) Accurate mass calc. for $C_{20}H_{38}NO_4Si$ (MH^+) 384.2570, obs. 384.2565. ^{1}H n.m.r. ($CDCl_3$) 4.35 (m H-1) 3.89 (t J=10.0 H-8) 3.72 (m H-6) 3.55 (dd J=3.6, 9.8 H-7) 3.19 (td J-6.7, 9.2 H-3) 3.17 (dd J=3.0, 14.8 H-5) 2.81-2.66 (m 3H H-3′, H-5′, H-8a) 2.02 (m H-2) 1.77 (m H-2′) 1.55-1.13 (m 11H cyclohexyl, -OH) 0.79, 0.02, 0.00 (s 9H, 3H and 3H TBDMS). ^{13}C n.m.r. ($CDCl_3$) 100.7, cyclohexylidene

quat.; 74.2 C-7; 72.3 C-6; 70.5 C-1; 64.1 C-8a; 63.3 C-8; 50.5, 50.4 C-5, C-3; 33.2 C-2; 36.9, 34.9, 25.4; 23.1; 22.9, cyclohexylidene; 25.7, 18.1, -4.3, -5.0; TBDMS.

6-*Epi*-castanospermine (112). A solution of the protected alcohol (111) (1.0 g, 2.6 mmol) in trifluoroacetic acid - water (7:3) (20 ml) was stirred at room temperature for 2 hr and then evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel (dichloromethane - methanol - aq. ammonium hydroxide (25% NH_3) 5:4:1). Fractions containing the product alcohol (112) were concentrated under reduced pressure, dissolved in water and passed through a column of ion exchange resin (Amberlyst A-26, OH form). Concentration to dryness under reduced pressure gave alcohol (112) (0.37 g, 1.95 mmol, 75%). Accurate mass, calc. for $C_8H_{16}NO_4$ (MH^+) 190.1079, obs. 190.1090. ^1H n.m.r. (D_2O) 4.45 (m H-1) 4.06 (bs H-6) 3.94 (t J=9.6 H-8) 3.59 (dd J=3.5, 9.5 H-7) 3.15 (m 2H H-3, H-5) 2.34 (m 2H H-2, H-5') 2.21 (q J=8.9 H-3') 1.98 (dd J=4.3, 9.7 H-8a) 1.78 (m H-2'). ^{13}C n.m.r. (D_2O) 78.1 C-7; 74.4 C-8a; 72.9 C-1; 71.6 C-6; 70.0 C-8; 58.0 C-5; 54.4 C-3; 35.5 C-2.

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