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Stereochemistry of Sapelin B; Correlation with Sapelin D. Anomalies in the Use of Shift Reagents for Determining the Absolute Configurations of α-Glycols

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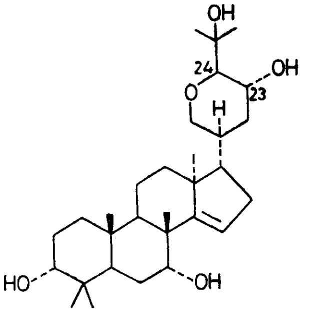
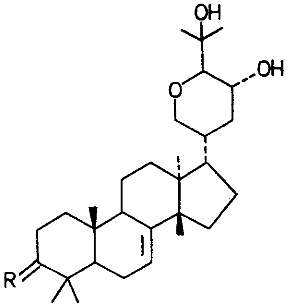
Summary The c.d. spectrum of sapelin B tribenzoate (**7**) and correlation with sapelin D (**1**) have shown sapelin B (**6**) to be 23*R*,24*S*, in agreement with their origin from a common biogenetic precursor; the c.d. spectra of sapelin B and methyl 4,6-*O*-ethylidene-α-D-glucopyranoside in the presence of Pr(dpm)$_3$ exhibit Cotton effects of opposite signs to those predicted.

The side chain of sapelin D (**1**)[1] was first encountered in bourjotinolone A (**2**)[2] and was assumed[2] to arise from the epoxydiol system (**4**). The same epoxydiol (**4**) could also give melianone (**5**)[3] and we have recently shown[4] that the stereochemistry of melianone (**5**) at C-23 and C-24 is, contrary to the initial assignments,[3] the same as in (**4**). The novel dihydroxyoxepan side chain in sapelin B (**6**)[5] is also derivable from the epoxydiol (**4**) and it is of interest to confirm the C-23 and C-24 stereochemistry assumed[5] for sapelin B (**6**) on these biogenetic grounds.

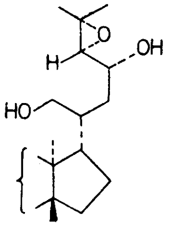
We have already shown[5] that the 23,24-glycol of sapelin B (**6**) is *trans*. Measurement of the c.d. spectrum of sapelin B (**6**) in the presence of Eu(dpm)$_3$ [or Pr(dpm)$_3$][6] would appear to be the most direct method of obtaining the absolute stereochemistry at C-23 and C-24. In the event, the c.d. spectrum of sapelin B (**6**) in the presence of either Eu(dpm)$_3$ or Pr(dpm)$_3$† gave a positive value for the longer wavelength (at 317 and 319 nm, respectively) Cotton effect.[6] This is contrary to what is expected for (**6**). However, the c.d. spectrum of sapelin B tribenzoate (**7**) (non-crystalline)‡ showed a negative Cotton effect ($\Delta\epsilon$ = −18 at 238 nm)† as expected for (**6**).[7]



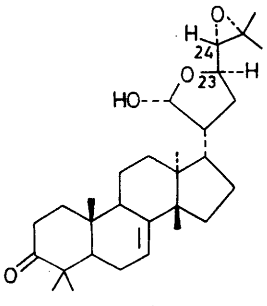
(1)



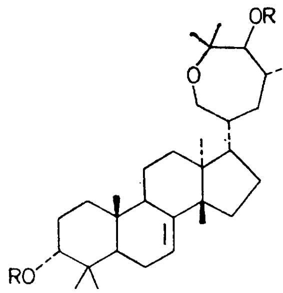
(2); R = O
(3); R = α-OH, H



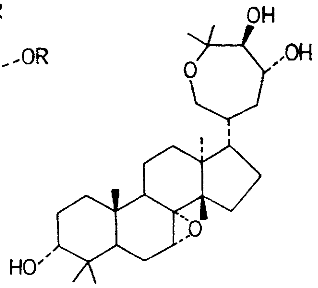
(4)



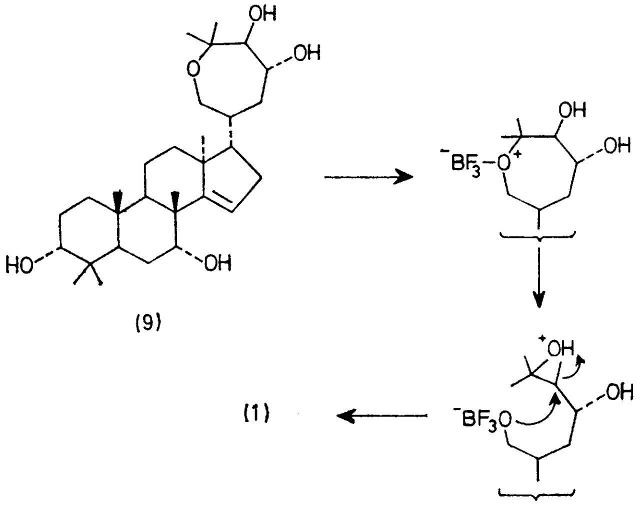
(5)



(6) R = H
(7) R = Bz



(8)



Scheme

The contradictory results obtained by the two chiroptical methods necessitated obtaining alternative evidence for the stereochemistry of sapelin B (**6**) and this was obtained as follows. Sapelin B (**6**) was converted into its 7α,8α-epoxide (**8**), m.p. 220–225 °C, using buffered *m*-chloroperbenzoic acid.[8] Rearrangement of the epoxide (**8**) with BF$_3$[1] gave a mixture of apo-sapelin B (**9**), m.p. 215—219 °C, and sapelin D (**1**), identical with authentic material.[1] Sapelin D (**1**) has been correlated[1] with sapelin A (**3**)[5] by

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† Measured at the University of Alberta.

‡ Satisfactory spectral data were obtained for all new compounds.

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reactions not involving the side chain. In our reported[5] correlation of sapelin A (**3**) with bourjotinolone A (**2**), the chirality at C-23 and C-24 was lost. We now report that, as expected, oxidation of sapelin A (**3**) with a limited amount of Jones' reagent gave a good yield of bourjotinolone A (**2**). Since the complete stereochemistry of bourjotinolone A (**2**) is known,[2] the above correlations define the stereochemistry of sapelin B (**6**) at C-23 and, since the α-glycol is *trans*, at C-24. The ring contraction is believed to proceed as outlined in the Scheme.

The chemical data show that the c.d. spectrum of sapelin B tribenzoate (**7**) leads to the correct chirality of the α-glycol whereas the use of shift reagents gives the wrong result. Another example of the failure of c.d. of an α-glycol complexed to a shift reagent to yield the correct chirality is provided by methyl 4,6-*O*-ethylidene-α-D-glucopyranoside whose c.d. spectrum in the presence of $Pr(dpm)_3$ gave a negative Cotton effect for the 314 nm (longer wavelength) band despite the positive chirality of the 2,3-glycol.

The dihydroxyoxepan side chain of sapelin B (**6**) also occurs in sapelin E,[1] which has been correlated with sapelin B (**6**), and in melianin B.[9] These and previous results[4] show that the four modifications of the highly oxidised tirucallol side chain represented by bourjotinolone A (**2**), melianone (**5**), sapelin B (**6**), and sapelin F,[4] which contains an acyclic tetrahydroxy side chain, are all derivable from the same precursor (**4**), and that the measurement of the c.d. of α-glycols in the presence of shift reagents is not always a reliable method for assigning their chirality.

We thank Professor G. Snatzke for obtaining the c.d. data of sapelin B in the presence of $Eu(dpm)_3$ and Professor R. U. Lemieux for a sample of methyl 4,6-*O*-ethylidene-α-D-glucopyranoside.

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