# Chiral Recognition in Complexes of Tertiary Acetylenic Alcohols and Sparteine; Mutual Optical Resolution by Complex Formation

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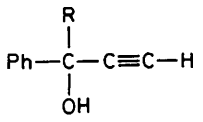
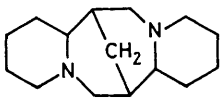
Tertiary acetylenic alcohols have been resolved efficiently by complex formation with (−)-sparteine, and (±)-sparteine was resolved by complex formation with the optically active tertiary acetylenic alcohols; an *X*-ray structural study of the 1:1 complex of 1-(*o*-bromophenyl)-1-phenylprop-2-ynol (**1d**) and (−)-sparteine showed that two hydrogen bonds, C≡C–H · · · OH and OH · · · N, are important in formation of the complex.

Previously, we have reported that brucine and tertiary acetylenic alcohols form crystalline complexes in which the alcohol recognises the chirality of brucine and hence the complexation can be used to resolve the acetylenic alcohol.[1] We now report that (−)-sparteine can be used instead of brucine for the optical resolution of the tertiary acetylenic alcohol (**1**), and that (±)-sparteine can also be resolved by complexation with optically active acetylenic alcohols.

When a solution of the propynol (**1c**) (12.5 mmol) and commercially available (−)-sparteine (12.5 mmol) in acetone (15 ml) was kept at room temperature for 12 h, a 1:1 (−)-sparteine complex of (−)-(**1c**) was formed as colourless prisms



(1)



sparteine

**a**; R = Bu$^t$
**b**; R = *o*-FC$_6$H$_4$
**c**; R = *o*-ClC$_6$H$_4$
**d**; R = *o*-BrC$_6$H$_4$

**Table 1.** Optical resolution of (**1a**—**d**) by one complexation with (−)-sparteine and brucine.

| | With (−)-sparteine | | | With brucine | |
|---|---|---|---|---|---|
| Enantiomer | Yield (%) | $[\alpha]_D$ (°) | %e.e. | Yield (%) | %e.e. |
| (−)-(**1a**) | 49 | −7.3 | 59 | 50 | 66 |
| (+)-(**1a**) | 51 | +7.1 | 57 | 48 | 71 |
| (−)-(**1b**) | 36 | −20.0 | 34 | 45 | 60 |
| (+)-(**1b**) | 61 | +13.9 | 23 | 52 | 53 |
| (−)-(**1c**) | 51 | −73.7 | 55 | 60 | 15 |
| (+)-(**1c**) | 44 | +81.3 | 60 | 38 | 22 |
| (−)-(**1d**) | 61 | −66.7 | 50 | 65 | 39 |
| (+)-(**1d**) | 37 | +109.0 | 81 | 35 | 81 |

(51%), m.p. 123—124 °C.† Decomposition of the complex with dil. HCl gave (−)-(**1c**), (51%), $[\alpha]_D$ −73.7°,† 55% enantiomeric excess (e.e.).† From the acetone solution, (+)-(**1c**) was obtained (44%), $[\alpha]_D$ +91.3°, 60% e.e. By the same procedure, (**1a**), (**1b**), and (**1d**) were also resolved easily (Table 1). In all cases, the sparteine complex of the (−)-enantiomer of (**1**) crystallised out. The m.p.s of the 1:1 sparteine complexes of (−)-(**1a**), (−)-(**1b**), and (−)-(**1d**) were 80—81, 121—122, and 129—130 °C, respectively.†

In some cases, optical resolution by complexation with sparteine is more efficient than that with brucine, and the use of the much less poisonous sparteine also has advantages over the use of the poisonous brucine. Furthermore, (−)-sparteine can easily be obtained by applying our resolution method to synthetic (±)-sparteine. 100% optically pure enantiomers of (**1**) could be obtained quite easily by repeating the recrystallisation of their (−)-sparteine complexes. For example, two recrystallisations from acetone of the (−)-sparteine complex prepared from 59% e.e. (−)-(**1a**) (1.49 g) gave 100% e.e. (−)-(**1a**) (0.80 g) after decomposition of the complex with dil. HCl. By the same procedure, 34% e.e. (−)-(**1b**) (2.00 g), 55% e.e. (−)-(**1c**) (1.56 g), and 50% e.e. (−)-(**1d**) (1.84 g) gave 85% e.e. (−)-(**1b**) (0.93 g), 100% e.e. (−)-(**1c**) (0.79 g), and 100% e.e. (−)-(**1d**) (0.91 g), respectively.

(±)-Sparteine which had been prepared by Leonard's method[2] was easily resolved by complexation with optically active acetylenic alcohols. For example, when a solution of 100% e.e. (−)-(**1d**) (1.66 g) and an equimolar amount of (±)-sparteine (1.35 g) in acetone (5 ml) was kept at room temperature for 12 h, a 1:1 sparteine complex of (−)-(**1d**) was formed as colourless prisms (24%). The complex was decomposed with dil. HCl, and from the HCl solution, (−)-sparteine was obtained as a colourless oil (24%), $[\alpha]_D$ −12.9°, 80% e.e. From the acetone solution, (+)-sparteine was obtained (74%), $[\alpha]_D$ +3.2°, 20% e.e. When the complexation of the 80% e.e. (−)-sparteine (0.32 g) and (−)-(**1d**) (0.40 g; 100% e.e.) was repeated again, 100% e.e. (−)-sparteine was obtained (0.26 g), $[\alpha]_D$ −16.4° (EtOH) {lit.[3] $[\alpha]_D$ −16.4° (EtOH)}. Similarly, following the complexation of the 20% e.e. (+)-sparteine (1.0 g) and (−)-(**1d**) (1.26 g; 100% e.e.) in acetone, 59% e.e. (+)-sparteine (0.47 g; $[\alpha]_D$ +9.4°) was obtained. This method seems to be applicable to the resolution of many other chiral polycyclic amines.

† All the m.p.s of the sparteine complexes correspond to those of 100% e.e. (**1**). All the $[\alpha]_D$ values were measured in MeOH (*c* 0.15) with a 1 dm cell at 25 °C, unless otherwise stated. All the e.e. values for (**1**) were determined by the same n.m.r. method in ref. 1.

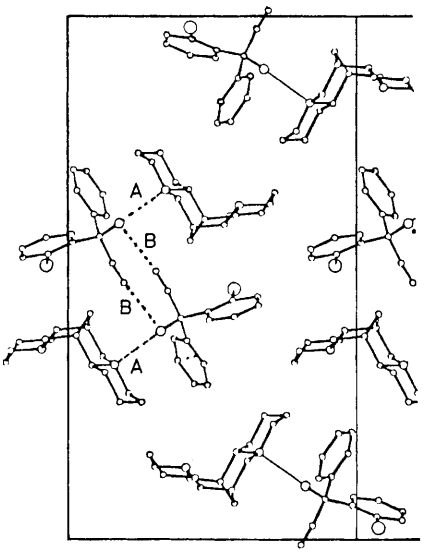



**Figure 1.** Packing diagram for the 1:1 complex of (−)-sparteine and (**1d**) showing two hydrogen bonds, O–H . . . N (A) and C≡C–H . . . OH (B).

In order to investigate how both components recognise so efficiently the chirality of each other in the complex, an *X*-ray analysis of the structure of the (−)-sparteine complex of (−)-(**1d**) was carried out.‡ The packing diagram (Figure 1) shows that two hydrogen bonds are important: one is between OH and N (A in Figure 1; distances between O and N, and H and N 2.70 and 1.80 Å, respectively; ∠O–H . . . N 165°) and the other is that between C≡C–H . . . OH (B in Figure 1; distances between C and O, and H and O 3.26 and 2.14 Å, respectively; ∠C–H . . . O 177°).

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‡ *Crystal data:* orthorhombic, space group $P2_12_12_1$ ($Z = 4$); $a$ = 13.498(2), $b$ = 24.283(6), $c$ = 8.156(2) Å. Data in an octant in reciprocal space was collected to $\sin\theta/\lambda = 0.61$ and 2942 intensities were recorded on a Rigaku AFC-5 diffractometer using monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71069 Å) and an $\omega/2\theta$ scan mode. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method to $R$ value of 0.068 for 2100 reflections with $F > 3\sigma(F)$. All H atoms were placed at their idealized positions.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.