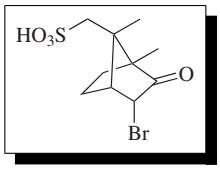
3-Bromocamphor-8-sulfonic Acid[1]



(1*S*)
[46472-20-2] $C_{10}H_{15}BrO_4S$ (MW 311.19)
InChI = 1/C10H15BrO4S/c1-9-4-3-6(7(11)8(9)12)10(9,2)5-16(13,14)15/h6-7H,3-5H2,1-2H3,(H,13,14,15)/t6-,7+,9+,10-/m0/s1/f/h13H
InChIKey = MFEDKMBNKNOUPA-XNYDDEHYDT

(1*R*)
[5344-58-1] $C_{10}H_{18}BrNO_4S$ (MW 328.22)
InChI = 1/C10H15BrO4S/c1-9-4-3-6(7(11)8(9)12)10(9,2)5-16(13,14)15/h6-7H,3-5H2,1-2H3,(H,13,14,15)/t6-,7+,9+,10-/m1/s1/f/h13H
InChIKey = MFEDKMBNKNOUPA-IIYQDPIPDR

(1*S*) (NH_4^+ salt)
[55870-50-3]
InChI = 1/C10H15BrO4S.H3N/c1-9-4-3-6(7(11)8(9)12)10(9,2)5-16(13,14)15;/h6-7H,3-5H2,1-2H3,(H,13,14,15);1H3/t6-,7+,9+,10-;/m0./s1/fC10H14BrO4S.H4N/h;1H/q-1;+1
InChIKey = GFBVBBRNPGPROZ-FSDGRROBDC

(1*R*) (NH_4^+ salt)
[14575-84-9]
InChI = 1/C10H15BrO4S.H3N/c1-9-4-3-6(7(11)8(9)12)10(9,2)5-16(13,14)15;/h6-7H,3-5H2,1-2H3,(H,13,14,15);1H3/t6-,7+,9+,10-;/m1./s1/fC10H14BrO4S.H4N/h;1H/q-1;+1
InChIKey = GFBVBBRNPGPROZ-AFZGIBLVDO

(±) (NH_4^+ salt)
[122519-23-7]
InChI = 1/C10H15BrO4S.H3N/c1-9-4-3-6(7(11)8(9)12)10(9,2)5-16(13,14)15;/h6-7H,3-5H2,1-2H3,(H,13,14,15);1H3/fC10H14BrO4S.H4N/h;1H/q-1;+1
InChIKey = GFBVBBRNPGPROZ-RHKOQSKFCT

(chemical resolutions;[1] starting material for the preparation of chiral reagents[2])

Alternate Names: α-bromocamphor-π-sulfonic acid; 3-bromocamphor-9-sulfonic acid.

Physical Data: free acid: mp 195–196 °C; (1*R*): $[\alpha]_D$ 88.3° (*c* 2.6, H_2O). NH_4^+ salt: mp 284 °C (dec); (1*R*): $[\alpha]_D$ 84.8° (*c* 4, H_2O)

Solubility: the ammonium salt is sol in water, slightly sol in EtOH, but essentially insol in acetone and Et_2O. The free acid is sol in EtOAc, MeCN, and 5% aq. NaOH.

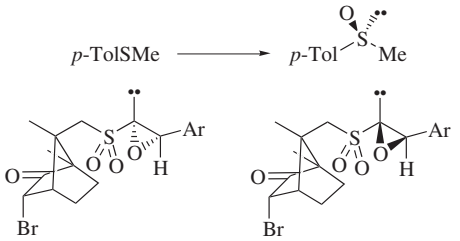
Form Supplied in: both enantiomers are commercially available as ammonium salts.

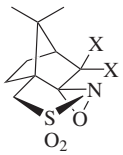
Preparative Methods: by sulfonation of bromocamphor with ***Chlorosulfonic Acid*** in $CHCl_3$.[3] Alternatively, fuming ***Sulfuric Acid*** can be used as both the solvent and sulfonating agent.[4] Recently, an improved preparation with an easier isolation procedure was reported (34% yield).[5] The acid can be prepared by passing a solution of the NH_4^+ salt in H_2O through a Dowex resin (H^+) column.[6] Alternatively, it can be obtained by adding ***Acetyl Chloride*** to a suspension of the ammonium salt in a 2:1 mixture of $CHCl_3$ and absolute EtOH.[7] The corresponding sulfonyl chloride is readily prepared from the acid or the NH_4^+ salt upon treatment with ***Phosphorus(V) Chloride*** and ***Phosphorus Oxychloride***.[8,9]

Purification: crystallized from H_2O.

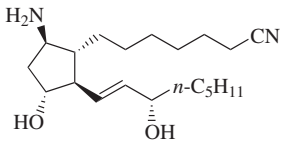
Handling, Storage, and Precautions: a 0.5 M solution of the free acid in dry MeCN is stable for at least 30 days at 5 °C in a closed vessel under N_2.[6]

Chemical Resolution of Compounds Containing Basic Groups. 3-Bromocamphor-8-sulfonic acid has been widely used as a resolving agent for compounds containing basic groups. A number of primary (**1**),[10] secondary (**2**),[11] and tertiary (**3**) amines[12] as well as oxazolines (**4**)[6] have been resolved by the formation of diastereomeric salts derived from 3-bromo-8-camphorsulfonic acid.

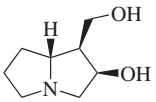




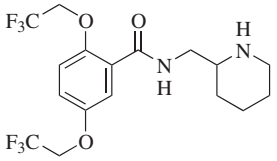
(**7**) X = H, 28% ee, (*S*), 80% yield
(**8**) X = Cl, 95% ee, (*S*), 95% yield



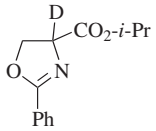
(**1**)



(**3**)



(**2**) Flecainide



(**4**)

The optical resolution of racemic *p*-hydroxyphenylglycine with 3-bromocamphor-8-sulfonic acid has also been achieved.[13] This resolving agent has also been widely used in the preparation of optically pure chromium[14] and cobalt complexes.[15]

Preparation of Chiral Reagents. 3-Bromocamphor-8-sulfonic acid has been used as a starting material for the synthesis

of chiral reagents.[16] Although the oxidation of sulfides to sulfoxides can be accomplished with the oxaziridine **5** or **6**, other camphor-derived oxaziridines (**7** and **8**) are the reagents of choice to accomplish this transformation (eq 1).[2–17]

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