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ALICYCLIC TERPENOIDS FROM CYCLOCITRYL PHENYL SULFIDES. II.

A SYNTHESIS OF DEOXYTRISPORONE

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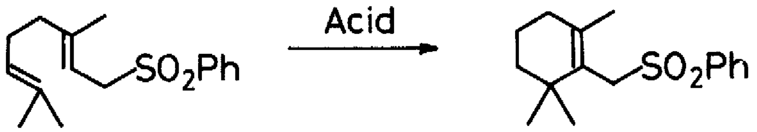
The development of a simple and practical method for preparation of functionalized cyclocitryl derivatives has long been received much interests since they would be promising versatile intermediates for synthesis of naturally occurring biologically active terpenoids such as vitamin A, abscisic acid and so on1) having the cyclocitryl moiety. In the last communication2) we demonstrated that sulfone (2) is effectively prepared by a simple process *via* sulfuric acid catalyzed cyclization of (1) and that it would become an useful key compound for the terpenoid synthesis as umpolung3) of cyclocitral. Here, as an efficient use of (2), we describe a novel synthesis of deoxytrisporone (3a)4), a sesquiterpene isolated from *Choanephora trispora*, a producer of β-carotene, trisporic A, B, and C acids, and trisporone.

Oxidation of (2) with SeO_2 in dioxane (80°, 1.5 hr) afforded alcohol (4, 74%)5). Treatment of (4) with 2 eq. of lithium diisopropylamide in THF (-78°, 10 min) followed by the action of methyl (2E)-3-methyl-4-bromo-2-butenoate6) and subsequent chromatography over SiO_2 gave (5) in 76% along with 22% of the starting material. Desulfonation7) of (5) with MeONa in *t*-BuOH at



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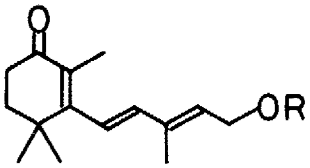
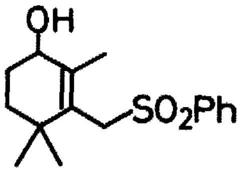


3a ; R=H , 3b ; R=CO(i-Pr)



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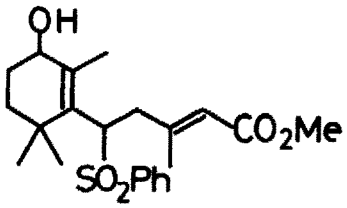

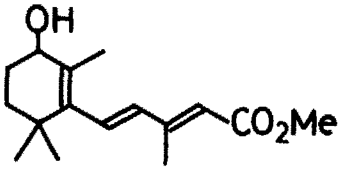

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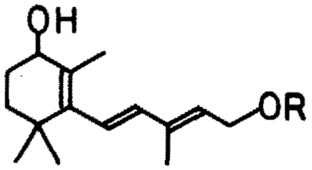

7a;R=H , 7b; R=CO(i-Pr)

room temperature underwent smoothly to yield (4E)-olefin (6, 90%), homogeneous in TLC and PMR. The PMR of (6) showed sharp two doublets at δ6.54 and 6.06 with J=17 Hz and gave no suggestion of presence of (4Z)-isomer. Reduction of (6) with $LiAlH_4$ in ether afforded diol (7a, 90%). Regioselective acylation of (7a) was performed in 90% by treatment with isobutanoic anhydride in pyridine. The monoester (7b) was oxidized with CrO_3 in pyridine at 15° to afford ketone (3b, 80%). Finally, deoxytrisporone (3a) was obtained quantitatively by hydrolysis of (3b) in KOH-MeOH at room temperature. Spectral data of (3a) was consistent with those reported$^{4)}$.

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