The Synthesis and Absolute Configurations of Lilac Alcohols

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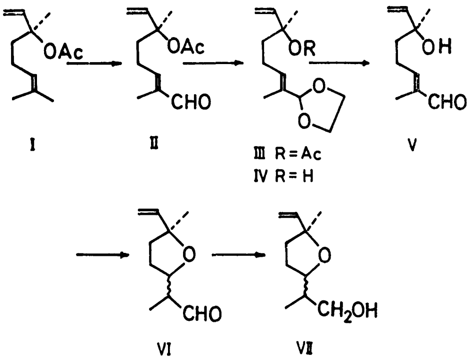
Lilac alcohols have recently been isolated and assigned to the diastereomers of β,5-dimethyl-5-vinyl-2-tetrahydrofuranethanol.[1,2] We now wish to describe a total synthesis of lilac alcohols with sufficient samples for the assignment of absolute and stereochemical configurations.



d-Linalyl acetate (I)[3] $[\alpha]_D^{25}$ +2.9 was treated with SeO_2 to afford α,β-unsaturated aldehyde II in 38% yield. Treatment of II with ethyleneglycol in the presence of *p*-toluenesulfonic acid in benzene gave ethyleneacetal III, which was hydrolysed with 5 N NaOH to afford IV. Column chromatography of IV on silica gel gave V (77% overall-yield from II to V).[4,5] The intramolecular Michael addition of alcohol to the α,β-unsaturated aldehyde was effected with NEt_3 to give VI in 43% yield. Reduction of VI with $LiAlH_4$ afforded a diastereomeric mixture (VII) of *d*-lilac alcohols in 75% yield. The mixture was separated completely by vpc to afford four diastereomers with R_t 7.1 $[\alpha]_D^{25}$ −1.4, 7.3 $[\alpha]_D^{25}$ +1.4, 8.8 $[\alpha]_D^{25}$ +6.7, and 10.1 $[\alpha]_D^{25}$ −0.5, which were shown to correspond to lilac alcohol-b, -d, -a, and -c, respectively, based on NMR, IR and optical rotations. *l*-Lilac alcohol-a $[\alpha]_D^{25}$ −11.6, -b $[\alpha]_D^{25}$ +3.0, -c $[\alpha]_D^{25}$ +2.5, and -d $[\alpha]_D^{25}$ −2.9 were synthesized from *l*-linalyl acetate[3] $[\alpha]_D^{25}$ −5.0 in a similar way, showing a contrary $[\alpha]_D$ to natural lilac alcohols. By combining the absolute configuration of *d*-linalool,[6] chemical relation to *trans*-linalool oxide,[1] and a detailed IR and NMR study of the intramolecular hydrogen bonding between the primary alcohol and ether linkage,[7] the absolute configurational assignments of lilac alcohol-a, -b, -c, and -d have been shown to be (βS, 2S, 5S), (βR, 2S, 5S), (βR, 2R, 5S), and (βS, 2R, 5S), respectively.

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[1] S. Wakayama, S. Namba, and M. Ohno, This Bulletin, **43**, 3319 (1970).

[2] S. Namba, S. Wakayama, and M. Ohno, The 14th Symposium of Perfume, Terpene, and Essential Oil, abstracts p. 60, Kitami, Japan (1970).

[3] This material was supplied by Takasago Perfumery Company. It was not perfectly pure optically, but proved to be pure enough to determine the absolute configuration.

[4] During the course of our synthetic work on lilac alcohols from linalool, Naegeli and Weber published the use of aldehyde (VI) as an intermediate to davanone synthesis. P. Naegeli and G. Weber, *Tetrahedron Lett.*, **1970**, 959.

[5] The direct hydrolysis of II gave V or VI in poor yield.

[6] R. H. Cornforth, J. W. Cornforth, and V. Prelog, *Ann. Chem.*, **634**, 197 (1960).

[7] The measurement of the intramolecular hydrogen bonding was carried out by IR and NMR.