Lilac Alcohol-a and -b, New Naturally Occurring Odorous Ingredients

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No constituents of lilac flower oil, *Syringa vulgaris* L. are known.[1] We could isolate and identify eighteen constituents from the oil obtained by steam distillation of the concrete (*n*-hexane extract of flowers). The main components which amount to 70 per cent of the oil have been found to be four new stereoisomeric terpene alcohols named lilac alcohol-a, -b, -c, and -d. They have the most exquisite floral fragrance. Lilac alcohol-a and -b have been assigned to the diastereomers of (2R, 5R)-β,5-dimethyl-5-vinyl-2-tetrahydrofuranethanol (I).

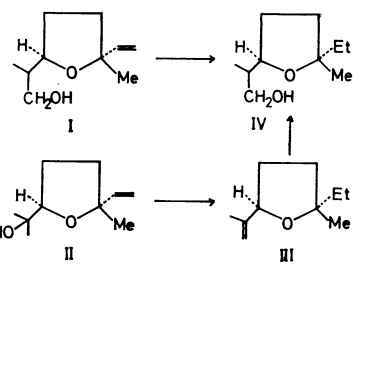
Lilac alcohol-a $[\alpha]^{25}_{D}+15.5°$ (c=0.515 in $CHCl_3$) and -b, $[\alpha]^{25}_{D}$ $-2°$ (c=0.535 in $CHCl_3$) have the same molecular formula $C_{10}H_{18}O_2$ (M^+, 170). The close similarity of their spectroscopic evidence such as IR, NMR and MS suggests that they are stereoisomers. The IR spectra show the presence of hydroxy (3520 cm^{-1}) and vinyl group (1640, 990, 920 cm^{-1}), and ether linkage (1015 cm^{-1}). The hydroxyl function has been shown to be primary by a prominent peak at *m/e* 31 (C^+H_2OH), and the presence of tetrahydrofuran ring has been shown by the characteristic α-fission of α-substituted tetrahydrofuran derivatives[2] (*m/e*, 155 $(M-CH_3)^+$; 143 $[M-(-CH{=}CH_2)]^+$; 111 $[M-(-CH\text{-}Me\text{-}CH_2OH)]^+$; 43 $CH_3{^+}C{=}O$). The NMR spectra (Table 1) of lilac alcohol-a and -b are reasonably consistent with the proposed structure (I).

A clear proof of the structure has been achieved by the transformation of lilac alcohols and *trans*-linalool oxide[3,4] (II) into the same derivative as shown below. Hydrogenation of II over Pt followed by acetylation and pyrolysis afforded 5-ethyl-2-isopropenyl-5-methyl-tetrahydrofuran (III), which gave a mixture of diastereomers of 5-ethyl-β,5-dimethyl-2-tetrahydrofuranethanol (IV) by hydroboration. Dihydrolilac alcohol-a and -b obtained by catalytic hydrogenation of I were confirmed to be identical with one diastereomer (Rt, 12.6 min) and another (Rt, 9.8 min) respectively.

TABLE 1. NMR SPECTRAL DATA
(δ in ppm, in $CDCl_3$)*

Lilac alcohol		a	b
s-CH_3		0.94 d J=6.0	0.80 d J=6.0
t-CH_3		1.31 s	1.30 s
$-CH_2-CH_2-$, $-\underset{H}{C}(CH_3)-$		1.82m	1.80m
$>\underset{H}{C}-CH_2OH$		3.66 (ABX)	3.62 (A_2X)
$>\underset{H}{C}-O-$		4.12m	3.80m
$H_3C{=}CH_1H_2$	H_1*	4.99	5.01
	H_2	5.17	5.19
	H_3	5.87	5.89

* The signals of alcohols appear at 2.96—2.60 δ, depending on the concentration, and typical signals of a vinyl group are observed with $J_{1,2}$=1.6 Hz, $J_{1,3}$=8.0 Hz and $J_{2,3}$=18 Hz.



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