BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(5), 1293—1294 (1974)

Lilac Aldehydes

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(Received November 8, 1973)

Synopsis. New odorous aldehydes, diastereomers, have been found in lilac flower oil and named lilac aldehydes. The structure was established to be 2-(1'-formyl)ethyl-5-methyl-5-vinyl tetrahydrofuran. Absolute configurations have also been inferred.

Odorous ingredients of lilac flower oil[1] and lilac alcohols,[2] naturally occurring odorous components, were previously reported.

This paper describes the isolation of aldehydic components having an excellent green tone and their identification as diastereomeric 2-(1'-formyl)ethyl-5-vinyltetrahydrofuran (I) by combined gas chromatography-mass spectometry.*

In the gas chromatogram (Fig. 1) three unidentified peaks subsequent to number 13 peak of linalool were the aldehydes having R_t 6.6, 7.3, and 8.5 min.

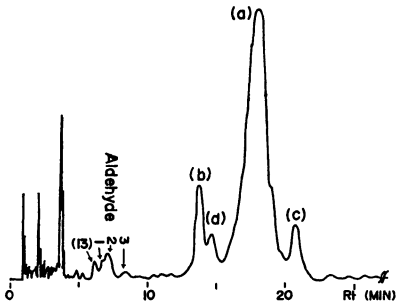


Fig. 1. Gas chromatogram of the lilac flower oil.
Column: 20% DEGS, 3 mm×3 m, Carrier Gas: He 30 ml/min, Oven Temp.: 120 °C, TCD

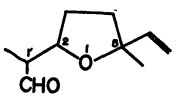
The mass spectra of the aldehydes are shown in Fig. 2; *m/e* 168 M^+, 153 $(M-CH_3)^+$, 141 $[M-(CH=CH_2)]^+$, 111 $[M-(CH\langle^{CH_3}_{CHO})]^+$, 55 $(CH_2=CH-C\equiv O)^+$, 43 $(CH_3-CO)^+$, 29 $(CHO)^+$. These fragments suggest structure (I) for the aldehydes.

In agreement with this formulation, R_t and mass spectra of the aldehydes synthesized from *d*-linalyl acetate were identical with those of natural aldehydes.

The structure of the aldehydes is comfirmed to be (I).

The aldehydes had been synthesized as intermediates for synthesizing lilac alcohols, but occurrence in nature has not yet been recorded. We wish to call them lilac aldehydes.

We intended to comfirm the absolute configurations



(I)

* Hitachi RM 50 GC, Ionization voltage 70 eV.

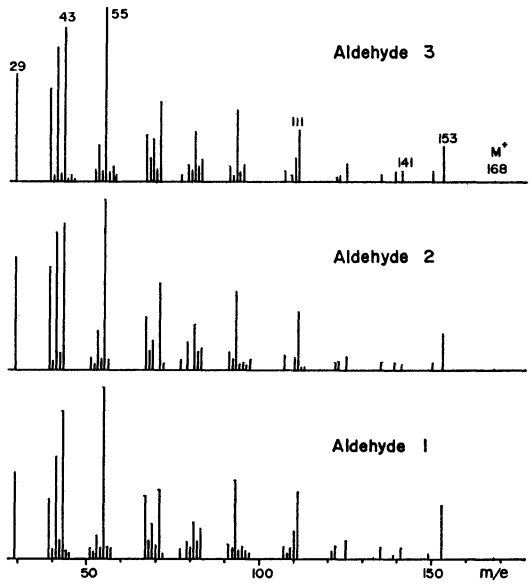


Fig. 2. Mass spectra of the lilac aldehydes.

of lilac aldehydes by converting them by reduction into lilac alcohols whose absolute configurations are comfirmed.** The gas chromatogram of the synthetic lilac aldehydes is shown in Fig. 3. Fractions corresponding to each peak were separated by repeated gas chromatography (PEG 20 M, 6 mm×5 m, 165 °C, He 45 ml/min). 2.4, 7.3, and 9.7 mg of d-2, d-3, and d-4 aldehydes, respectively, were reduced with $LiAlH_4$ to give the alcohols. The gas chromatograms of the alcohols are shown in Fig. 4. Judging from R_t and mass spectra, the alcohols were confirmed to consist of lilac alcohol-a, -b, -c, and -d.

Natural lilac aldehyde fraction exhibiting three peaks in gas chromatogram were reduced in the same manner as in synthetic aldehydes. The derived alcohols were also a mixture of the four diastereomeric lilac alcohols (Fig. 4).

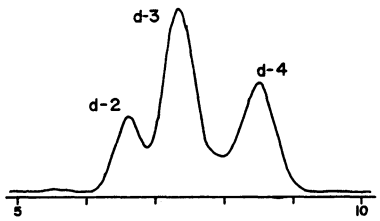


Fig. 3. Gas chromatogram of the synthetic *d*-lilac aldehydes.
Columun: 20% DEGS, 3 mm×3 m, carrier gas: He 30 ml/min, oven temp.: 120 °C, TCD.

** Since *d*-lilac alcohols in lilac flower oil amount to 70 per cent, lilac aldehydes would be *d*-series in view of biogenesis.[2] Due to too small amount of available natural aldehydes, measurements of $[\alpha]_D$ have not been carried out.

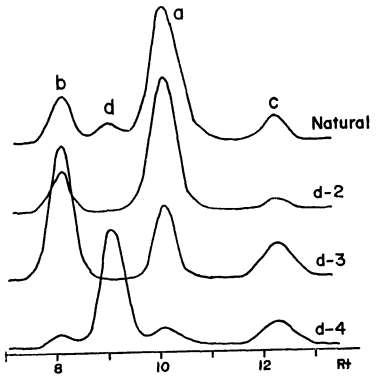


Fig. 4. Gas chromatograms of the reduced alcohols of natural and synthetic aldehydes.
Column: 15% DEGS, 3 mm×2 m, carrier gas: He 30 ml/min, oven temp.: 130 °C, TCD.

Although synthetic as well as natural lilac aldehydes showed only three peaks in gaschromatograms due to too small difference of R_t in two isomers, they were found to be a mixture of four diastereomers just as in lilac alcohols.

In the process of separation by liquid chromatography on alumina, it is interesting that natural lilac aldehydes were eluted in ether fraction, while synthetic lilac aldehydes were eluted in benzene–hexane (1: 1) fraction in the same manner as usual carbonyl compounds. Such an anomaly in natural lilac aldehydes seems to be due to an interaction between lilac aldehydes and abundantly existent lilac alcohols.

The characteristic greenish tone of the lilac flower seems to be duplicated by adding lilac aldehydes to lilac alcohols. This might also be ascribed to the interaction between the alcohols and the aldehydes.

References

1) S. Wakayama, S. Namba, and M. Ohno, *Nippon Kagaku Zasshi*, **92**, 256 (1971).

2) S. Wakayama, S. Namba, and M. Ohno, This Bulletin, **43**, 3319 (1970); S. Wakayama, S. Namba, K. Hosoi, and M. Ohno, *ibid.*, **44**, 875 (1971); **46**, 3183 (1973).