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TRIALKYLTRIOXANES IN FLOWER WAX OF SOME DECORATIVE ROSES

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Abstract—The polymeric form in which long-chain aliphatic aldehydes are present in rose flower waxes has been established as the 2,4,6-trialkyl 1,3,5-trioxane.

INTRODUCTION

As early as 1959 Lamberton and Redcliffe [1] established for the first time the presence of aldehydes in plant waxes, and they were faced by the question about the form in which they occurred in plants. As the most feasible form they suggested the polymeric trioxane type but were unable to confirm their existence in sugar-cane wax [2], where free aldehydes constitute about 50% of the wax. However, on the basis of the behaviour of dodecanal in aqueous solution, studied by Klass *et al.* [3], Lamberton suggested that aldehydes in plants may occur as hemihydrates which during the course of wax isolation, are converted into free aldehydes.

In studying the wax composition of three decorative roses (*Rosa americana, R. imperial* and *R. virgo*), we established the presence of aldehydes [4]. In the group separation of these waxes, we isolated a substance with an R_f value, different from that of the frequently found components of the waxes. From its behaviour, we suspected the compound to be a polymeric form of the aldehydes and the present paper reports our results from the study of this compound.

RESULTS AND DISCUSSION

In the group separation of the waxes from the three roses on a Si gel column and after monitoring the eluate by TLC, we noted that the last hydrocarbon fractions eluted with hexane, contained in addition to hydrocarbons, another substance 1a, which migrated between the hydrocarbons and the palmitone standard. It was isolated by PLC and repeatedly chromatographed. However, it was found that it always contained a more polar component 1b, irrespective of the fact that we scraped off only one band from the preparative separation. For this reason, our attempts to purify this substance on Si gel proved unsuccessful and it was obvious that it underwent a change during the course of chromatography. By recrystallization from EtOH, it was obtained in a pure state according to TLC and IR data, but during its storage we again established the presence of the polar component. A larger amount of 1b was isolated by PLC from the mother liquor when 1a was recrystallized. The IR-spectrum of 1b indicated the presence of an aldehyde. These results suggested that the isolated substance 1a could be a polymeric form of the aldehydes, which were contained in all three waxes and that a partial depolymerization occurred when placed on Si gel or on storage. Further investigations confirmed that assumption. The IR of 1a showed an ether bond at 1115 cm^{-1}, the remainder of the spectrum being similar to that of long-chain hydrocarbons. There were no absorption bands for unsaturation or carbonyl functions. No unsaturation was established by TLC on Si gel–$AgNO_3$. The PMR of 1a indicated an unsymmetrical triplet for trioxane ring protons [5]. This signal excludes a linear aliphatic ether, whose ether protons are always in a higher field. Me protons occurring as an unresolved triplet at δ 0·90, methylene protons in an α-position to the trioxane ring protons as a broad peak at δ 1·6, and a large CH_2-peak at δ 1·2 were present in the PMR spectrum of 1a. No aldehyde proton was observed. Assuming three trioxane ring protons per molecule, all spectroscopic evidence showed that the average number of carbon atoms of 1a was about 60. The GLC analysis of this substance indicated a series of peaks, while with the aid of GC–MS we showed that the main peaks were due to even-numbered long-chain unsaturated alcohols and to odd-numbered long-chain paraffins. The contradiction between the MS-data and those from IR, PMR and TLC for 1a suggested that it underwent thermal decomposition during GLC. However, the MS identification of unsaturated alcohols, and the fact that the signal observed in PMR fell in the region for olefinic protons, prompted us to check again whether 1a possessed any unsaturation. Accordingly, a part was subjected to catalytic hydrogenation and the reaction product was studied by TLC after

Table 1. Composition (%) of free and bound aldehydes (as trialkyltrioxanes) in flower wax of *Rosa imperial*

Carbon number	Aldehydes from trialkyltrioxanes	Free aldehydes
14	3·6	—
15	0·1	—
16	3·0	2·0
17	0·1	0·4
18	—	1·1
18	2·5	4·3
19	1·3	2·2
20	7·8	10·3
21	6·1	9·7
22	27·3	30·1
23	4·3	7·6
24	20·0	15·5
25	2·2	2·4
26	11·2	7·1
27	1·1	1·1
28	9·4	6·2
29	—	—
30	—	—

48 hr. Instead of a more nonpolar product, we established a strongly polar one, identical in R_f to octadecanol. We also established paraffins in an insignificant amount. The main part of the starting material was unchanged. After extending the duration of the reaction, we again established, with the aid of TLC, that the amounts of the starting material and of the alcohols decreased, while the amount of paraffins increased. After complete conversion of **1a**, the two reaction products (alcohols and paraffins) were separated by PLC. Their composition was established by GLC and their chain lengths corresponded with those of the free aldehydes [4] in rose wax.

The slow change of **1a** during hydrogenation and the identification of paraffins and alcohols as reaction products confirmed our assumption for the polymeric form of aldehydes of a trioxane type. A slow depolymerization occurs under the conditions of hydrogenation and the aldehydes obtained are reduced to alcohols and partially to hydrocarbons.

Taking into account the studies carried out by Horvat *et al.* [7], in which the trialkyl trioxanes, obtained from autoxidized methyl linoleate were depolymerized to aldehydes, we subjected **1a** to a similar treatment. The aldehydes freed were purified by PLC from the side products in the reaction (acetals and aldol condensation and subsequent dehydration products of aldehydes) [7]. The aldehydes from the trialkyl trioxanes were reduced with $LiAlH_4$ to alcohols and their acetates were analyzed by GLC. The data from the analysis are given in Table 1. A very good agreement is observed between the aldehydes obtained from the trialkyl trioxanes and the free aldehydes. The C_{22} and C_{24} homologues are prevalent in both fractions.

EXPERIMENTAL

Chromatography. TLC and PLC were carried out on Si gel plates. The plates were developed in the systems (A) $CHCl_3$–hexane (0·1:9·9), (B) Et_2O–hexane (0·2:9·8), (C) C_6H_6–hexane (3:7), (D) C_6H_6–hexane (1:1), (E) hexane–Et_2O–MeOH (4:2:0·1).

During preparative stages, zones on plates were located by spraying with Rhodamine 6G and observation under UV light. The bands were scraped off from the plates immediately after development and eluted with Et_2O.

Isolation of trialkyl trioxanes (**1a**). The isolation of waxes from three varieties of decorative (*R. americana*, *R. imperial* and *R. virgo*) was as described earlier [6]. TLC in system A showed that hydrocarbons from all three roses contained a more polar compound **1a** in a small amount. It was isolated by PLC in the same system and comprised about 2·1–2·2% of the total wax in all three roses. **1a** (R_f 0·73) was found to contain an impurity **1b** (R_f 0·31) in system C. It was rechromatographed in systems B, C and D. Recrystallization from EtOH yielded pure **1a**. **1b** was isolated from the mother liquor after PLC in system C. IR of **1a**: $\nu_{max}^{CCl_4}$ 1115 cm^{-1}. IR of **1b**: $\nu_{max}^{CCl_4}$ 1732 and 2724 cm^{-1}. PMR of **1a** (100 MHz, $CDCl_3$, internal standard TMS): δ 0·90 (9H, unresolved *t*), 1·2 (120 H, *s*), 1·6 (6 H, *m*) and 5·01 (3 H, *t*).

Hydrogenation of **1a** (6·5 mg) was effected with PtO_2 in HOAc. After 120 hr the reaction product was isolated. TLC in hexane showed paraffins (R_f 1·0) and another substance at the start. The latter had R_f equal with that of a long-chain primary alcohol in systems D and E. By PLC in system E 2·2 mg of paraffins and 2·5 mg of alcohols were isolated.

Depolymerization of **1a** (5 mg) was carried out with 3M HCl in 30% MeOH in a sealed tube at 110° for 4 hr [7]. The aldehydes from the depolymerization (R_f 0·31) were purified from two substances (R_f 0·47 and R_f 0·90) by PLC in system C. After purification the aldehydes (2·4 mg) gave single spots in different systems. Reduction of the aldehydes from **1a** to alcohols was carried out using the method of ref. [8]. Their acetate derivatives were purified by PLC in system D.

GLC. The paraffin and alcohols from the hydrogenation of **1a** were chromatographed on 1·5% SE-30 and 1·5% OV-17 columns, respectively. Acetylated alcohols from aldehydes of **1a** were analyzed on a glass column (1·5 m × 3 mm) packed with 3% OV-17, temp. programmed from 150 to 260° at 4°/min, N_2 at 32 ml/min.

GC–MS of **1a** was performed on 3% SE-30, temp. programmed 145 to 250° at 2°/min, ionizing energy 70 eV.

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