Phytochemistry, 1969, Vol. 8, pp. 1549 to 1552. Pergamon Press. Printed in England.

COMPOSITION, STRUCTURE AND BIOGENESIS OF THE KETONES IN ROSE FLOWER WAX

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(*Received* 11 *February* 1969)

Abstract—A homologous series of aliphatic ketones from C_{17} to C_{35} has been found in the flower wax of *Rosa damascena* Mill. Ketones with an even and odd number of carbon atoms, with a straight chain and with methyl groups as side chains are present. The percentage compositions in terms of chain length and C-methylation are correlated with those of the paraffins and fatty acids of the wax and suggest a biogenetic relationship between the ketones and the other hydrocarbon constituents.

INTRODUCTION

EARLIER,[1] we showed on the basis of i.r. spectral data, the preparation of oximes and their Beckmann rearrangement products, that at least six higher ketones are present in wax of rose flowers, *Rosa damascena* Mill. According to the NMR spectral data, the carbonyl group of these ketones was not in position 2. We then assumed [1]that the number of ketones might be larger and that there was probably a homologous series present, by analogy with the hydrocarbon series in the same wax.[2] In view of their biogenetic interest,[3,4] we decided to study the composition and the structure of ketones in rose flower wax in more detail. Since direct gas–liquid chromatography (GLC) of the ketones is not possible because of their high boiling points—above 400° (and since a preliminary pyrolysis would produce results similar to Beckmann rearrangements) we reduced the ketones to the hydrocarbons and identified them by GLC. We also carried out a mass spectral investigation of the ketone mixture.

RESULTS

The GLC results on the hydrocarbons formed on reduction are given in Table 1. As can be seen, the wax contains a homologous series of all the nineteen ketones from C_{17} to C_{35} with even and odd numbers of carbon atoms. The ketones with an odd number of carbon atoms, particularly C_{31}, C_{29}, C_{27}, C_{19} and C_{33}, are represented in a considerably greater amount than those with an even number of carbon atoms. We noticed in the GLC trace a splitting of the peak of C_{33} and chromatography of a larger sample of the mixture showed a similar splitting of the peaks C_{27}, C_{30} and C_{32}. This splitting of the peaks can only be caused by the presence

[1] B. STOIANOVA-IVANOVA, P. HADJIEVA and K. MLADENOVA, *Riv. Ital. E.P.P.O.S.* **49**, 12 (1967).
[2] V. WOLLRAB, M. STREIBL and F. SORNY, *Collection* **30**, (5) 1654 (1965).
[3] A. C. CHIBNALL, S. H. PIPER, A. POLLARD, Y. A. SMITH and E. F. WILLIAMS, *Biochem. J.* **25**, 2095 (1931).
[4] D. R. KREGER *Encyclopaedia of Plant Physiology*, Vol. 10, p. 249, Springer, Berlin (1958).

TABLE 1. GLC DATA ON THE QUANTITATIVE COMPOSITION OF KETONES AND PARAFFINS FROM ROSE FLOWER WAX (mol%)

Number of carbon atoms	Ketones	Paraffins*
17	0·4	0·1
18	0·2	0·1
19	3·4	2·6
20	1·0	0·4
21	2·9	3·6
22	1·0	0·2
23	2·3	2·9
24	1·2	0·4
25	2·4	2·6
26	2·2	0·6
27	6·8	17·7
28	2·8	2·3
29	8·3	21·0
30	2·8	1·3
31	55·5	32·8
32	2·6	0·8
33	3·2	10·6
34	1·2	
35	0·8	

* The data on paraffins are taken from Wollrab.[6]

TABLE 2. MASS SPECTRAL DATA OF KETONES OF ROSE FLOWER WAX

Number of carbon atoms	$\frac{(M-15)^+}{M^+}$	Structure of carbon chain
17	0	Normal
18	3·1	Branched and normal
19	3·9	Branched and normal
20	1·9	Branched and normal
21	0	Normal
22	3·5	Branched and normal
23	0	Normal
24	1·8	Branched and normal
25	6·2	Branched and normal
26	14·3	Branched and normal
27	3·4	Branched and normal
28	1·4	Branched and normal
29	0	Normal
30	6·2	Branched and normal
31	0	Normal
32	32·0	Mainly branched

of branched-chain hydrocarbons with the same number of carbon atoms. It cannot be due to unsaturated hydrocarbons because, before GLC, the mixture was separated from unsaturated compounds on a silica gel–silver nitrate column; also the mass spectra shows no M-2 peaks.

The mass spectral examination of the ketone mixture (Table 2) confirmed the above results. As the fragmentation under electron impact of higher ketones has not been studied so far, we assumed that the ketones would behave similarly to the higher paraffins.[5] It has been shown that paraffins with a straight chain give a very intensive molecular peak, while the peak $(M-15)^+$ is lacking and the relationship $(M-15)^+/M^+$ is close to zero. When a methyl group is present as side chain, the ratio of abundances $(M-15)^+/M^+$ is about 3. When two and more methyl groups are present, this ratio is higher. For five of the ketones (Table 2), this ratio is zero so that we can assume that the ketones C_{17}, C_{21}, C_{23}, C_{29} and C_{31} have a normal structure and are not admixtures with branched-chain ketones. For all the other ketones, the ratio $(M-15)^+/M^+$ is greater than zero, an indication of the presence of ketones with side-chain methyl groups. The percentage of branched-chain ketones appears to be considerable. As the mixture studied by mass spectrometry contains at the same time normal ketones and branched-chain ketones, no more definite conclusions about the structure of the ketones can be drawn from the ratio $(M-15)^+/M^+$. The large ratio $(M-15)^+/M^+=32$ for the ketone C_{32}, however, shows with certainty that its main component is the branched-chain ketone, containing probably a quaternary hydrocarbon atom. The fact that the GLC gives data for branched ketones only for C_{25}, C_{30}, C_{32} and C_{33}, whereas the mass spectrum shows that eleven branched ketones are present, can be explained by the insufficient selectivity of the liquid phase for the separation of the normal and branched-chain hydrocarbons.

DISCUSSION

No reliable data are so far available on the content of unsymmetrical ketones in plant waxes.[4] The fact established by us that in rose flower wax there are ketones with even-numbered carbon atoms is simultaneously a proof for the presence of unsymmetrical ketones in it. A comparison of our results on the ketone composition in rose flower wax with those of the composition of paraffin hydrocarbons in the same wax given by Wollrab,[6] is shown in Table 1. Significantly, the distribution curve for ketones and hydrocarbons fully coincides in the C_{17}–C_{26} range; in the C_{27}–C_{32} range the amount of hydrocarbons rises abruptly, and only at C_{31} is the ketone prevalent. The fact that the hydrocarbons in the largest amount correspond to the ketones represented in the highest amount is further evidence for a biogenetic relationship between ketones and hydrocarbons (c.f. Ref. 3). Our discovery of ketones containing one or more methyl groups in the side chain, compares very well with the results obtained by Wollrab *et al.*[2] for the presence of monomethyl- and dimethylparaffins in rose flower concrete.

Quantitative correlations between the ketone and the fatty acids of the wax are also apparent from our results. Thus, the large amount of the C_{31} ketone compares with the high content of palmitic acid in rose flower wax,[7] while the insignificant quantity of the even-numbered ketones can be related to the low content of odd acids, needed for their formation.

[5] K. Biemann, *Mass-Spectrometry—Organic Chemical Applications*, p. 78, McGraw Hill, New York (1962).
[6] V. Wollrab, *Collection* **33**, (5), 1584 (1968).
[7] B. Stoianova-Ivanova and K. Mladenova, *Riv. Ital. E.P.P.O.S.* **50**, 72 (1968).

However, our results, especially the lack of ketones containing carbonyl groups in position 2, do not agree with Kreger's[4] scheme for the formation of the C_{29} ketone in plant waxes by ω-oxidation of palmitone, followed by β-oxidation, decarboxylation and reduction.

EXPERIMENTAL

Isolation of Ketones

Ketones were isolated by column chromatography of rose flower (*Rosa damascena* Mill.) concrete wax on Al_2O_3 with elution by benzene–ether. Their purity was assayed by an i.r. spectrum and TLC.

Reduction of Ketones

The reduction of the ketones to hydrocarbons was carried out after Clemmensen.[8] The degree of reduction was followed up by i.r. spectrum. The hydrocarbon mixture was chromatographed on a column of silica gel–Ag NO_3 with elution with petroleum ether.

Gas–Liquid Chromatography

A Perkin Elmer F 11 Gas Chromatograph equipped with flame ionization detector was used. The spiral glass 1·8 m long column was packed with SE-30 silicon on Chromosorb W (80–100 mesh). The instrumental conditions: 8°/min temperature programme ran from 200 to 275°; N_2 carrier gas, flow rate 14 ml/min. Standards: C_{22}, C_{24}, C_{28}, C_{32} and C_{36}.

Mass Spectral Study of the Ketones

The mass spectrum was taken at the Institute de Chemie—Strasbourg—Laboratoire de Chimie Organique. Temperature: 180°, with a low ionizing energy.

[8] E. L. MARTIN, *J. Am. Chem. Soc.* **58**, 1438 (1936).