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SHORT COMMUNICATION

THE COMPOSITION AND STRUCTURE OF KETONES FROM ROSE BUD AND ROSE FLOWER WAXES

B. STOIANOVA-IVANOVA and K. MLADENOVA
Department of Chemistry, Sofia State University, Sofia, Bulgaria
and
S. POPOW
Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

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Abstract—No considerable changes occur in the composition of wax ketones during the development of rose buds into flowers. Mass spectral data show that the ketone present in the largest amount in the waxes is the unsymmetrical hentriacontan-9-one and that 2-methyl C_{30}, C_{28}, C_{27} and C_{26} ketones also occur. From the results obtained, compared with those by other authors, a biogenetic relationship is suggested between paraffins, olefins, secondary alcohols and ketones in the rose flower wax.

INTRODUCTION

EARLIER work[1] established that Bulgarian rose flower (*Rosa damascena* Mill.) wax contains long-chain *n*-ketones. In later work[2] a homologous series of ketones from C_{17} to C_{35}, in which odd carbon-numbered compounds prevailed, was identified by hydrogenation of the ketones to hydrocarbons, gas–liquid chromatography (GLC) of the hydrogenated product and study of the mass spectrum of the ketones. Hentriacontanone was found in the largest amount, the presence of *iso*ketones was shown, and a biogenetic relationship was suggested between acids, ketones and hydrocarbons in the wax. Because the ketone mass spectrum was effected at a low ionizing energy, no information was obtained about the position of the carbonyl group.

In this paper, the qualitative and quantitative compositions of the ketones in the waxes of rose buds and flowers picked simultaneously from the same plants are compared with a view to elucidating the biogenetic relationship between the acids, primary and secondary alcohols, ketones and hydrocarbons of the waxes. By applying mass spectrometry at a high ionizing energy the structure of the ketones and the position of the carbonyl group were determined.

RESULTS

Ketones from waxes of rose bud and rose flower of the same plants were isolated by the procedure described earlier.[1] After purification from traces of esters and alcohols accompanying them, the ketones were hydrogenated by the method of Clemmensen.[2] The hydrogenated products (hydrocarbons), after being purified from alcohols and olefins (side products in the reduction) by the method described in,[2] were analysed by GLC. The results are given in Table 1.

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[1] B. STOIANOVA-IVANOVA, P. HADJIEVA and K MLADENOVA, *Riv. Ital. E.P.P.O.S.* **49**, 12 (1967).

[2] B. STOIANOVA-IVANOVA, P HADJIEVA and S POPOW, *Phytochem.* **8**, 1549 (1969)

TABLE 1. GLC DATA ON THE QUANTITATIVE COMPOSITION OF THE KETONES FROM ROSE BUD AND ROSE FLOWER WAX

Number of carbon atoms	%	
	Rose buds	Rose flowers
C_{27}	1 7	1 9
C_{28}	0 6	3 0
C_{29}	7 6	7 4
C_{30}	1 2	1 6
C_{31}	83 1	79 8
C_{32}	3 1	3 4

During the development of the bud into a flower no significant changes in the quantitative and qualitative composition take place.

The mass spectral study of the ketones, isolated from bud and flower wax has confirmed this result: the ketones of the two samples are identical qualitatively and very similar quantitatively. The main component is the $C_{30}H_{62}CO$ ketone (mol. wt. 450). The mass spectral data indicate that it is not *n*-hentriacontan-16-one (palmitone), but an isomer with a different position for the carbonyl group. According to Beynon *et al.*[3] for the asymmetrical ketones a stronger intermolecular reaction $M^+ + H$ is more characteristic than for the symmetrical ketones. In point of fact, the ratio $M/M + 1$ for palmitone is 3, while in the case of our ketone, this ratio is 2·66.

To determine the position of the carbonyl group, the peaks for α- and β-splitting were sought. While in palmitone the α-splitting produces a maximum at *m/e* 239 (the transition 450–239 is confirmed by a metastable peak with *m/e* 127·5), in this case this peak is absent, while the peaks at *m/e* 337 and *m/e* 141 are present (the transition 450–337 is confirmed by a metastable peak with *m/e* 252·2). This α-splitting may be explained only by the following structure of the ketone studied:

$$C_8H_{17}\text{—}CO\text{—}C_{22}H_{45}.$$

Actually, peaks with *m/e* 113 (C_8H_{17}) and with *m/e* 309 ($C_{22}H_{45}$) are found in the spectrum, which are also due to the α-splitting.

The β-splitting likewise confirmed this structure. There are peaks at *m/e* 352 and *m/e* 156 in the spectrum, while in the case of palmitone this splitting leads to a fragment with *m/e* 254.

The two carbon chains are normal, which follows from the slight intensity of the peaks $M^+ - 15$ and $M^+ - 29$ as compared with the molecular peak. The weak peaks at *m/e* 239 (α-splitting) and *m/e* 254 (β-splitting) make it possible to assume that the ketone mixture studied contains about 1–2% palmitone

The mass spectral data at a high ionizing energy confirm that in the case of the ketones which are a mixture of normal and branched, the latter contain a methyl group as a side chain[2] Moreover, these data now indicate more definitely that the branched ketones C_{30}, C_{28}, C_{27} and C_{26} contain this group in the 2 position (*iso*propyl group). The mass spectra study again confirmed that the C_{32} ketone is most markedly branched[2]

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[3] J H. Beynon, G. R. Lester, K. A. Saunders and A E. Williams, *Trans. Faraday Soc.* **57**, 1259 (1961)

DISCUSSION

Until recently it was believed that only symmetrical ketones[4] are present in plant waxes The only exception was nonacosan-10-one, found first in the wax on the stem of *Laserpitium latifolium*,[5] and then in the surface lipid from leaves of *Brassica oleracea*.[6] The detection, by mass spectroscopy at a low ionizing energy, of ketones with even-numbered carbon atoms in rose flower wax[2] is an indirect proof of the occurrence of unsymmetrical ketones. The presence of hentriacontan-9-one in the same wax is further proof of the occurrence of unsymmetrical ketones in plant waxes.

On the basis of a comparison of percentage contents in rose flower wax, we concluded that a biogenetic relationship exists between ketones and paraffins.[2] By comparing the distribution curves of ketones and secondary alcohols isolated from Bulgarian rose flower wax we also suggested a probable biogenetic relationship between ketones and secondary alcohols.[7] If Wollrab's data on the composition of secondary alcohols[8] are compared with our data on the composition of the ketones, it is seen that hentriacontan-9-one (88·4%) predominates among the secondary alcohols and hentriacontan-9-ol (79·8%) among the ketones. These results suggest a biogenetic relationship between the paraffins, secondary alcohols and ketones of rose wax. Furthermore, nonadecan-9-ene occurs in the greatest amount in the olefins from stearoptene of Bulgarian rose oil.[9] The fact that the functional group is also in the 9 position in the ketones and secondary alcohols present in the largest amounts in the wax may indicate a biogenetic relationship between the paraffins, secondary alcohols, ketones and olefins.

The finding[10] that the labelled primary alcohol (1-^{14}C)-1-hexacosanol and the symmetrical ketone (15-^{14}C)-15-nonacosanone do not lead to the formation of labelled normal hydrocarbons may be explained by the probable participation of secondary alcohols with an odd number of carbon atoms and their corresponding unsymmetrical ketones in the biogenesis of the normal odd-numbered hydrocarbons, which are the main component of wax from rose flower.

EXPERIMENTAL

Purification of the Ketones Isolated

The ketones isolated were purified on an Al_2O_3 column by gradient elution with benzene–$CHCl_3$ The ketone fraction was eluted by benzene–$CHCl_3$ (1 4) Their purity was assayed by TLC on silica gel-gypsum with petroleum–benzene (4 1)

Gas–Liquid Chromatography

A Shimadzu GC1c Gas Chromatograph equipped with flame ionization detector was used. The 1·11 m long column is packed with SE 30 10% on Chromaton N (0 14–0 25 mm) Carrier gas N_2, flow rate 50 ml/min Temperature programme 4°/min from 40 to 300°

Mass Spectral Study of the Ketones

The mass spectra were taken at an Electro Dynamic Co. apparatus in the National Chemical Laboratory, Poona, India Ionizing energy 70 eV temperature of the ion source 200°.

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[4] D R KREGER, *Encyclopaedia of Plant Physiology*, Vol 10, Springer, Berlin (1958).

[5] S HUNECK, *Naturwiss* **47,** 160 (1960).

[6] S J. PURDY and E V. TRUTER, *Proc Roy Soc B.* **158,** 553 (1963)

[7] B STOIANOVA-IVANOVA, P HADJIEVA and S GERGOVA, *Riv Ital E P P O S* in press

[8] V WOLLRAB, *Collection* **34,** 867 (1969)

[9] B STOIANOVA-IVANOVA and E IGNATOVA, *Riv Ital E P P O S* **51,** 375 (1969)

[10] L MONDESHKY, B STOIANOVA-IVANOVA, G ZOLOTOVIC and N MAREKOV, *Compt Rend Acad Bulgare Sci* **22,** 679 (1969)