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NONACOSANE-5,8-DIOL: A NEW COMPONENT OF PLANT WAXES

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Abstract—A new fraction has been isolated by chromatographic methods from the wax of the Bulgarian oil-bearing rose According to its IR, NMR and MS it was characterized as an homologous series of γ-diols, from C_{17} to C_{33} with the major homologues those containing an odd number of carbon atoms Nonacosane-5,8-diol is the major constituent

INTRODUCTION

THE BIOGENESIS of hydrocarbons in plant waxes is still in dispute and data have been gathered in favour of one or another hypothesis.[1,2] This problem is associated with the study of the composition of plant waxes, and for many years, we have investigated the composition of the wax from the Bulgarian oil-bearing rose. This contains straight chain components, such as hydrocarbons, olefins and conjugated dienes,[3] primary and secondary alcohols,[4] unsaturated secondary alcohols,[5] unsaturated and saturated acids,[6] ketones,[7,8] γ-lactones[9] and others. Rose flower wax has also been studied by Wollrab.[10,11] The results obtained suggested the existence of some biogenetic relationships, e.g. between unsaturated and saturated hydrocarbons, and between unsaturated and saturated secondary alcohols, and ketones.[5,11] On this basis the presence of conjugated dienes in the rose wax suggests the existence of diols in the wax and they are identified in the present work.

RESULTS AND DISCUSSION

TLC of the benzene–alcoholic and alcoholic eluates obtained from column chromatography of rose flower wax revealed spots which corresponded to substances more polar

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[10] WOLLRAB, V (1968) *Coll Czech Chem Commun* **33**, 1584
[11] WOLLRAB, V (1969) *Phytochemistry* **8**, 623

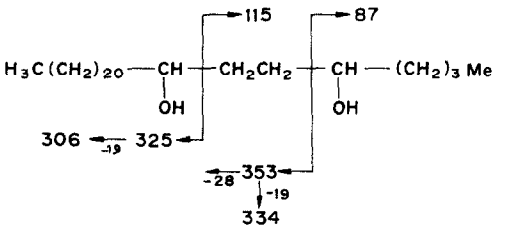
than primary alcohols. One of them had the same R_f as that of a higher aliphatic glycol IR showed a maximum for a secondary OH group at 1100 and 3640 cm^{-1}, as well as an intense band for a hydrogen bond in the region 3200–3500 cm^{-1}, indicating a diol group. The NMR of this fraction showed signals for Me protons at 0·9$^{\delta}$, a CH_2 signal centered at 1·3$^{\delta}$, a $C\underline{H}_2CHOH$ (*m*) at 1·4$^{\delta}$, an OH (*s*, *br*, 2H) at 2·1$^{\delta}$ and for $C\underline{H}OH$ (*m*, 2H) at 3·45$^{\delta}$. The NMR of the acetate derivative showed signals for Me (*tr*, *J* 6·5 Hz) at 0·85$^{\delta}$, CH_2 at 1·28$^{\delta}$, $C\underline{H}_2CHOH$ (*m*) at 1·47$^{\delta}$, $O\underline{Ac}$ (2*s*, 6H) at 2·05$^{\delta}$ and 2·06 and for $C\underline{H}OAc$ at 5·02$^{\delta}$ (*m*, 2H).

The MS of the fraction showed the presence of an homologous series of straight chain diols from C_{17}–C_{33}. The observation of Beynon[12] that the most intense ions in the MS of diols arise from cleavage α to the hydroxyl groups served as a basis for its interpretation The MS also shows hydrocarbon fragments C_nH_{2n+1} and C_nH_{2n-1} as well as M-18 ions. The diols with an odd number of carbon atoms are the major constituents with the diol C_{29} predominant. This was confirmed by a comparison with the MS of the acetylated product and by GLC analysis of the hydrocarbons prepared by reduction Accurate mass measurement at high resolution of the M^+ of the C_{29} and C_{31} homologues also showed that they corresponded to diols (Table 1)

TABLE 1 MS FRAGMENTS SUBJECTED TO HIGH RESOLUTION ANALYSIS

m/e	Experimental mass	Deduced empirical formula	Calculated mass
468	468 4888	$C_{31}H_{64}O_2$	468 4906
440	440 4552	$C_{29}H_{60}O_2$	440 4593
	440 3615	$C_{30}H_{48}O_2$	440 3654
353	353 3763	$C_{24}H_{49}O$	353 3783
334	334 3583	$C_{24}H_{46}$	334 3599
325	325 3469	$C_{22}H_{45}O$	325 3470

The MS of the diol fraction was sufficient to deduce the structure of the predominant C_{29} diol The high abundance of the ions M-115 at *m/e* 325 (10% of the base peak at 69) and M-87 at *m/e* 353 (10) is an indication of a γ-position of both hydroxyl groups i e nonacosane-5,8-diol



Further proof of this structure is the ratio between the abundances of the peaks at *m/e* 115 (9·7), 101 (9·7), 87 (51·6) and 73 (9·7) which is exclusively in favour of the ion 87 Further fragmentation of the ions *m/e* 325 and 353, with a loss of mass 19, results in the ions 306 (10·6) and 334 (9·7) respectively. This pattern of fragmentation was supported by the presence of metastable peaks at *m/e* 289 and 317 for the transitions 325→306 and 353→334

[12] BEYNON, J H, SAUNDERS, R A and WILLIAMS, A E (1968) *The Mass Spectra of Organic Molecules* p 151, Elsevier, New York

respectively and also by accurate mass measurement of the ions *m/e* 353, 334 and 325 (Table 1). The ion *m/e* 325 is also derived from *m/e* 353 by the loss of *m/e* 28. The high molecular weight of diols did not allow a GC–MS investigation of their TMS ether derivatives.

The ester fraction isolated by column chromatography of rose wax was saponified in order to establish whether diols are present in an esterified form. The TLC of the isolated neutral product did not show the presence of diols. The diols are therefore similar to the secondary alcohols of the wax in occurring only in a free form.[5,11]

Up to now no γ-diols have been established in natural waxes (of plant or animal origin) although α,β, α,ω and $\alpha,(\omega-1)$ diols have been found in other natural waxes.[13–25]

The presence in rose wax of an homologous series both of conjugated dienes and γ-diols in which the homologues with an odd number of carbon atoms predominate suggests a biogenetic relationship between them. It is well known that in plant waxes the acids and the primary alcohols are present mainly with an even number of carbon atoms, the biogenetic relationship between them having been proved experimentally. Other components of plant waxes such as hydrocarbons, secondary alcohols and ketones are present as homologues mainly with an odd number of carbon atoms, and a biogenetic relationship also exists between them. To these latter compounds one should now add γ-diols. The fact that α,β and α,ω-diols are present in plant waxes chiefly with an even number of carbon atoms whereas the γ-diols are present with an odd number suggests a different pattern for their biogenesis.

EXPERIMENTAL

Rose blossom wax (38 g) was chromatographed on a column of basic Al_2O_3 using gradient elution with C_6H_6–Et_2O The course of elution was monitored by TLC on silica gel G, solvent systems with an increasing polarity were used The diol references used were the α,β-diols obtained from oxidation of the olefin fraction of the wax with a per-acid. The isolation of the investigated substance in a chromatographically pure state (7% of the rose wax) was achieved by preparative TLC using $CHCl_3$ of the column fractions obtained by elution with C_6H_6–Et_2O (1 2) After recrystallization from MeOH the substance gave m p 71–72° Conversion to the hydrocarbons was carried out according to Downing *et al* [16] The product obtained was analysed by GLC on a column of 1 5% SE 30 on Chromosorb W (60–80 mesh) at 100–300° Acetylation was carried out using the method of Stransky [25] IR were measured in CCl_4 soln NMR were determined in $CDCl_3$ with TMS as internal standard at 100 MHz The MS of the diols and their acetyl derivatives were determined on a LKB 9000 instrument at 70eV High resolution measurements were made on a MS 9 instrument

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