MASS SPECTRA OF LONG-CHAIN ALIPHATIC β-DIKETONES AND SOME OF THEIR DERIVATIVES

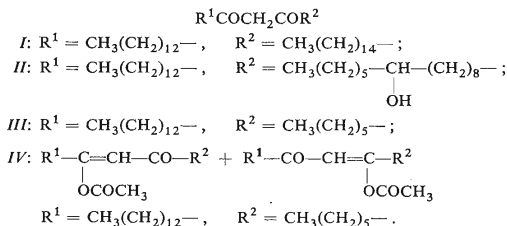A.Trka and M.Streibl

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In connection with the analysis of rye straw wax, the mass spectra of two natural compounds, 14,16-hentriacontanedione (*I*) and 25-hydroxy-14,16-hentriacontanedione (*II*), and of two synthetic model compounds, 7,9-docosanedione (*III*) and its enol-acetate (*IV*) were examined. On the basis of high-resolution measurement of *I—IV*, the fragmentation of long-chain aliphatic β-diketones could be explained and a fragmentation pattern designed for aliphatic hydroxy--β-diketones with a long chain.

By analysis of rye straw leaf wax, two long-chain aliphatic diketones, 14,16-hentriacontanedione (*I*) and 25-hydroxy-14,16-hentriacontanedione (*II*) were isolated and identified and their mass spectra were measured[1]. The interesting and novel findings from the analysis of these two mass spectra and those of two model substances, 7,9-docosanedione (*III*) and its enol-acetate (*IV*), are presented here.

$$R^1COCH_2COR^2$$

I: $R^1 = CH_3(CH_2)_{12}—,$ $R^2 = CH_3(CH_2)_{14}—;$

II: $R^1 = CH_3(CH_2)_{12}—,$ $R^2 = CH_3(CH_2)_5—CH—(CH_2)_8—;$
                                              $\underset{OH}{|}$

III: $R^1 = CH_3(CH_2)_{12}—,$ $R^2 = CH_3(CH_2)_5—;$

IV: $R^1—\underset{\underset{OCOCH_3}{|}}{C}=CH—CO—R^2 + R^1—CO—CH=\underset{\underset{OCOCH_3}{|}}{C}—R^2$

$R^1 = CH_3(CH_2)_{12}—,$ $R^2 = CH_3(CH_2)_5—.$

EXPERIMENTAL

Fig. 1

Mass Spectra and Fragmentation Schemes of 7,9-Docosanedione (A), 14,16-Hentriacontanedione (B) and 25-Hydroxy-14,16-hentriacontanedione (C); Direct inlet, electron energy 70 eV

296, $C_{19}H_{36}O_2$; 281, $C_{18}H_{33}O_2$; 278, $C_{19}H_{34}O$; 268, $C_{17}H_{32}O_2$; 253, $C_{16}H_{29}O_2$; 250, $C_{17}H_{30}O$; 239, $C_{16}H_{31}O$; 235, $C_{16}H_{27}O$; 220, $C_{16}H_{28}$; 211, $C_{14}H_{27}O$; 192, $C_{14}H_{24}$; 138, $C_9H_{14}O$; 100, $C_5H_8O_2$; 71, C_5H_{11}; 43, C_3H_7 (85%), C_2H_3OO(15%). 25-Hydroxy-14,16-hentria-contanedione (*II*): 480, $C_{31}H_{47}O_3$; 395, $C_{25}H_{47}O_3$; 366, $C_{26}H_{46}O_2$; 348, $C_{24}H_{44}O$; 312, $C_{19}H_{36}O_3$; 307, $C_{20}H_{35}O_2$; 297, $C_{18}H_{35}O_3$; 294, $C_{19}H_{34}O_2$; 279, $C_{18}H_{31}O_2$; 276, $C_{19}H_{32}O$; 237, $C_{16}H_{29}O$;236, $C_{16}H_{28}O$;233, $C_{17}H_{29}$;218, $C_{16}H_{26}$;198, $C_{12}H_{22}O_2$;183, $C_{11}H_{19}O_2$(70%), $C_{13}H_{27}$(6.3%); 180, $C_{12}H_{20}O$; 169, $C_{10}H_{17}O_2$(2.7%), $C_{12}H_{25}$(20%). Composition of the ions *m/e* 281, 268, 253, 250, 211, 192, 138, 100 and 43 under *I*. 7,9-Docosanedione (*III*): 338, $C_{22}H_{42}O_2$; 183, $C_{11}H_{19}O_2$; 170; $C_{10}H_{18}O_2$; 155, $C_9H_{15}O_2$; 152, $C_{10}H_{16}O$; 113, $C_7H_{13}O$(68%), $C_6H_9O_2$(17%); 94, C_7H_{10}; 85, C_6H_{13}(16.3%), $C_4H_5O_2$(13.2%), C_5H_9O(3.5%). Composition of the ions *m/e* 281, 268, 253, 250, 235, 211, 192 and 43 under *I*. 7,9-Docosanedione enol-acetate (*IV*): 380, $C_{24}H_{44}O_3$; 295, $C_{18}H_{31}O_3$; 208, $C_{14}H_{24}O$; 197, $C_{11}H_{17}O_3$. Other ions under *III*.

Synthesis of 7,9-docosanedione. The novel diketone was prepared by Claisen's acylation of 2-octanone with methyl tetradecanoate using sodium hydride[2] in a 59% yield (crude). The product was purified *via* cupric salt[3] and recrystallized from ethyl acetate; m.p. 34—34.5°C. According to the IR spectrum it contained mostly the enol form (1 605 cm^{-1}) and a small amount of the keto form (1700, 1 725 cm^{-1}). For $C_{22}H_{42}O_2$ (338·6) calculated: 78·04% C, 12·51% H; found: 77·88% C, 12·35% H. The acetylation was performed with acetic anhydride in pyridine at room temperature. The compound obtained (*IV*) was chromatographically homogeneous.

RESULTS AND DISCUSSION

The mass spectra of *I* (Fig. 1, *B*) and of *II* (Fig. 1, *C*) were examined on the basis of high resolution measurements. It was found that the fragmentation processes of aliphatic β-diketones with a long chain resemble in many features the analogous fragmentation of lower β-diketones[4,5] and that, using their low resolution mass spectra, the number of carbon atoms in both alkyls can be determined. The spectrum of the hydroxy derivative *II* carries some features of the spectrum of unsubstituted β-diketone but, in addition, it contains significant peaks corresponding to the presence of an alcoholic function in the molecule and making it possible to determine
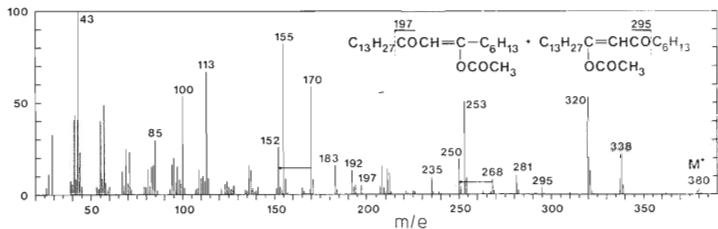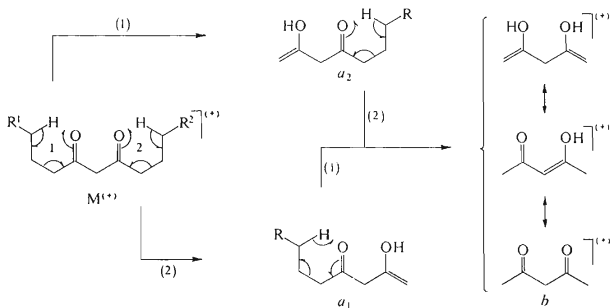

FIG. 2

Mass Spectrum and Partial Fragmentation Scheme of a Mixture of Both Tautomeric 7,9-Docosane-dione Enol-acetates

Direct inlet, electron energy 70 eV.

unequivocally its position, as will be shown below. For the sake of comparison and support of interpretation of the spectra of *I* and *II*, the spectrum of synthetic *III* (Fig. 1, A) and *IV* (Fig. 2) was also analyzed.

As shown in Figs 1*A*, *B* and *C*, one of the most prominent peaks in the lower region of β-diketone spectra occurs at m/e 100, corresponding to ion b of elementary composition $C_5H_8O_2$. The ion was observed earlier[4,5] in spectra of lower β-diketones when one of the alkyls was methyl and the ion was formed by β-elimination of the longer alkyl by McLafferty rearrangement. With higher β-diketones bearing sufficiently long alkyls (at least C_3) the ion b is formed by a successive β-elimination of both alkyls with two McLafferty rearrangements (Scheme 1).

The ion CH_3CO^+ formed by α-splitting from the b ion[4,5] represents in case of the compounds under study about 15% of the base peak. Relatively abundant peaks, corresponding to ions c_1 or c_2 (R_1—$COCH_2CO^+$ and R_2—CH_2CO^+), a_1 or a_2 (Scheme 1) and d_1 or d_2 (formed by splitting off a molecule of water from a_1 and a_2) form in the middle region of the spectrum readily distinguishible groups (Fig. 1) that can be used for identifying alkyls R^1 and R^2. Further decomposition of d_1 and d_2 proceeds by elimination of an acetone molecule, giving rise to unsaturated ions e_1 and e_2 of elementary composition $C_{n+1}H_{2n-2}$ (n being the number of carbon atoms in the β-diketone alkyl). The more important fragmentation processes of β-diketones include α-cleavage of C—C bond between the two carbonyls, leading to the[4,5] acylium ions f_1 and f_2, elimination of the larger radical being preferred. Loss of the CO molecule from this ion could be detected only in the spectrum of the lightest β-diketone *III* (Fig. 1, *A*: m/e 113 → 85, $m^+/e = 63.9$). In addition to the α- and β-cleavage, γ-cleavage is observed in all cases (ions g_1 and g_2), yielding low- or medium-intensity

SCHEME 1

peaks (Fig. 1). The molecular group of lower intensity in mass spectra of *I* and *III* shows the $[M-1]^+$ ion. The spectrum of hydroxy derivative *II* displays in addition to it an ion $[M-2]^+$ of approximately the same intensity.

The origin of the prominent peak at m/e 395 in the mass spectrum of *II* cannot be explained by simple α-cleavage, caused by charge localization on the alcoholic hydroxyl group, since in such a case the favoured α-elimination of the heavier part of the molecule would have to proceed at least to the same yield, thus forming an oxonium ion of mass 115. The absence of the peak at m/e 115 in the spectrum of *II* and, on the other hand, the presence of some other peaks (m/e 366, 348, 198, 183, 169) could be explained on the basis of a cyclic fragmentation mechanism, similar to that proposed by McCloskey and coworkers[6] for rationalizing the decomposition pathway of long-chain hydroxy esters.

The cyclic fragmentation mechanism of hydroxy-β-diketones assumes the localization of positive charge on M$^+$ at the nearer (Scheme 2) oxygen of the diketo group (with respect to the alcoholic function) and a transfer of hydrogen from the alcoholic hydroxyl, giving rise to an oxonium ion h or h′ by loss of the alkyl radical (path 1), or to a neutral molecule of aldehyde (path 2). The ion h (Scheme 2) splits off a molecule of methyl ketone to yield an ion i (peak at m/e 169). The oxonium radical j, arising from path 2, would be rather unfavourable energetically and therefore it is
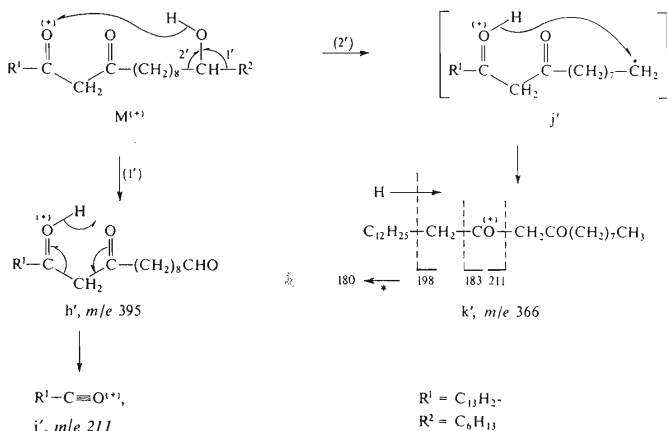

SCHEME 2

supposed to change immediately into the ion k (which can be taken for a molecular ion of the corresponding shorter-chain β-diketone) by hydrogen transfer from the oxonium oxygen to the carbon radical end of the species j. This explanation is supported also by the fact that the spectrum does not contain a sufficiently intense peak at m/e 140, corresponding to the ion that should arise from decomposition of species j by the same mechanism as proposed here for the formation of i from h. The great difference in abundances of peaks at m/e 395 and 366 indicates the decomposition of M^+ by path 1 to be strongly preferred. (The suggested general cyclic fragmentation mechanism of long-chain aliphatic hydroxy β-diketones is presented on the example of fragmentation of 25-hydroxy-14,16-hentriacontanedione). Decomposition of M^+ with a charge localized at the more distant oxygen (Scheme 3) yields through path 1' an acylium ion i', with splitting off a keto aldehyde molecule. The same ion, forming the peak at m/e 211, originates also in simple α-splitting from M^+, just as with β-diketones I and III. The greater intensity of the peak at 211 in the spectrum of II as compared with that of I and III can thus be due to the simultaneous occurrence of the two fragmentation processes.

In agreement with the above fragmentation path according to Scheme 2 and 3 it was possible to determine the position of the hydroxyl in the molecule of hydroxy β-diketone and to confirm that compound II possesses the structure of 25-hydroxy-14,16-hentriacontanedione, as originally assumed.

SCHEME 3

The mass spectrum of 7,9-docosanedione enol-acetate (*IV*, Fig. 2) resembles that of the nonacetylated β-diketone *III*. This is due to the fact that the molecular ion of enol-acetate readily loses a ketene molecule to yield a molecular ion of the corresponding β-diketone. The most abundant peak of the upper part of the spectrum of *IV* (m/e 320, 53% of b.p.) is formed through elimination of CH_3COOH from the M^+ of enol-acetate or of water from the M^+ of the β-diketone. Both corresponding metastable transitions are visible in the spectrum. Decomposition of ions at m/e 338 and 320 gives then rise to the characteristic patterns of the spectrum of the β-diketone *III*. In addition, the spectrum of *IV* contains some other peaks, relating directly to decomposition of the molecular ion (*e.g.*, m/e 295 and 197, Fig. 2). It follows from the above said that the mass spectrum of a mixture of both isomeric enol-acetates of β-diketone which could not be resolved may be equally readily interpreted as the spectrum of the parent compound and can be used for its identification.

We are indebted to Mr K. Konečný for technical assistance.

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Note added in proof: Recently two papers hawe appeared [Dieriskx P. J., Buffel K.: Phytochemistry *11*, 2654 (1972) and Tulloch A. P., Hoffman L. L.: Lipids *8*, 617 (1973)], where the basic electron impact induced fragmentation of three isomeric 5-, 6- and 7-hydroxy-14,16-hentriacontanediones has been described.