CHEMICAL IONIZATION MASS SPECTRA OF NATURAL MONOHYDROXY- AND MONOACYLOXY-SUBSTITUTED DIHYDROPYRANOCOUMARINS AND DIHYDROFUROCOUMARINS

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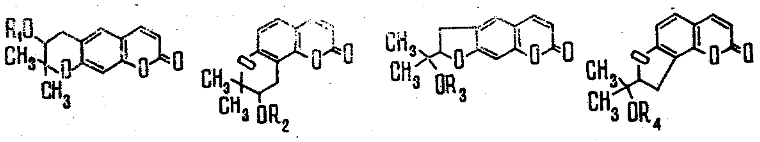
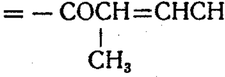
The fragmentation under electron impact (EI) of natural monohydroxy- and monoacyloxy-substituted dihydropyranocoumarins and dihydrofurocoumarins has been studied previously [1-4]. In the present paper we consider the fragmentation of this class of compounds (I-X) under the conditions of chemical ionization (CI) in order to determine the features of their fragmentation by this method in comparison with electron impact and to determine the structural and analytical possibilities of the method of chemical ionization in this series of compounds.



I $R_1 = -H$, II $R_2 = -H$, III $R_1 = -COC(CH_3) = CHCH_3$, IV $R_2 = -COC(CH_3) = CHCH_3$, V $R_3 = -H$, VI $R_4 = -H$, VII $R_3 = -COCH_3$, VIII $R_3 = -COC(CH_3) = CHCH_3$, IX $R_4 = -COC(CH_3) = CHCH_3$, X $R_3 =$



$$= -\underset{\displaystyle CH_3}{COCH}=CHCH_3$$

Below we give the chemical ionization mass spectra of compounds (I-X) and the stability of the quasimolecular ions Q^+ (W_{Q^+}) (the mass numbers of the ions are given in m/e and their intensities in percentages of the maximum peak are shown in parentheses):

Agasyllol (I)

288(0.8), 287(4.0), 277(0.4), 276(1.5), 275(8.5), 257(0.3), 250(0.5), 249(3.5), 248(15.5), 247(100), 246(5.4), 245(0.3), 231(0.4), 230(0.4), 229(2.3), 203(0.9), 187(1.2), 177(0.4), 176(0.4), 175(2.7). $W_{Q^+} = 80\%$.

Xanthogalol (II)

288(0.7), 287(3.5), 277(0.9), 276(1.4), 275(8.0), 257(0.3, 250(0.3), 249(2.9), 248(15), 247(100), 246(5.8), 245 (1.2), 231(0.5), 230(0.8), 229(5.6), 203(0.3), 176(0.3), 175(0.2). $W_{Q^+} = 84\%$.

Agasyllol angelate (III)

371(1.2), 370(3.6), 369(11.8), 359(2.2), 358(8.0), 357(29.8), 355(0.4), 346(0.8), 345(3.2), 343(0.7), 332(1.8), 331(10.1), 330(40.2), 329(100), 328(5.0), 327(0.7), 319(0.6), 318(2.1), 317(10.6), 275(0.8), 269(0.7), 257(2.2), 248(0.8), 247(5.0), 231(1.0), 230(4.0), 229(25.0), 228(6.2), 213(1.7), 83(1.9). $W_{Q^+} = 70\%$.

Xanthogalol angelate (IV)

371(0.4), 370(1.8), 369(7.0), 359(0.6), 358(3.6), 357(14.1), 355(0.2), 343(0.2), 332(0.4), 331(3.6), 330(21.4), 329(100), 328(4.2), 327(1.1), 247(0.2), 230(0.4), 229(3.0), 228(0.4), 213(0.1), 83(0.9). $W_{Q^+} = 92\%$.

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Marmezin (V)

289(0.2), 288(1.5), 287(7.8), 277(0.5), 276(3.5), 275(19.1), 273(0.2), 261(0.2), 257(0.9), 250(0.2), 249(2.4), 248(16.4), 247(100), 246(5.5), 231(0.3), 230(1.4), 229(9.7), 203(0.1), 188(0.3), 187(0.4). $W_{Q^+} = 87\%$.

Columbianetin (VI)

288(0.7), 287(3.7), 276(1.3), 275(8.1), 269(0.5), 257(1.7), 250(0.3), 249(2.6), 248(14.8), 247(100), 246(5.6), 245(0.7), 231(1.6), 230(6.0), 229(39), 228(1.1), 227(0.4), 217(2.0), 215(0.6), 188(0.6), 187(3.0). $W_{Q^+} = 63\%$.

Marmezin acetate (VII)

331(0.2), 330(1.1), 329(5.8), 319(0.4), 318(2.9), 317(15.2), 303(0.2), 292(0.3), 291(2.9), 290(17.4), 289(100), 288(3.3), 287(0.2), 275(0.4), 269(0.3), 258(0.2), 257(1.2), 248(0.3), 247(2.2), 231(2.7), 230(2.7), 229(1.8), 228(1.8), 213(0.4). $W_{Q^+} = 81\%$.

Marmezin angelate (VIII)

370(0.9), 369(2.8), 359(0.7), 358(2.4), 357(10.1), 355(0.7), 332(1.3), 331(5.9), 330(21.7), 329(100), 328(3.7), 327(0.7), 287(0.7), 275(0.9), 269(0.9), 259(0.9), 258(0.7), 257(2.8), 249(0.7), 248(1.3), 247(7.0), 246(0.7), 245(0.7), 244(0.7), 232(0.9), 231(4.2), 230(11.2), 229(72), 228(9.6), 227(1.1), 215(0.9), 214(0.7), 213(2.2), 203(0.7), 187(2.2), 83(11). $W_{Q^+} = 43\%$.

Columbianetin angelate (IX)

371(0.7), 370(3.4), 369(13.1), 359(1.2), 358(7.4), 357(30), 355(0.4), 331(3.6), 330(21), 329(100), 328(9.6), 327(1.6), 257(1.0), 231(1.2), 230(9.3), 229(60), 228(3.0), 83(0.6). $W_{Q^+} = 59\%$.

Marmezin cis-3-methylthioacrylate (X)

389(0.4), 388(1.0), 387(4.3), 378(0.2), 377(1.2), 376(3.4), 375(14.5), 373(0.1), 361(0.3), 351(0.1), 350(1.3), 349(8.3), 348(21.4), 347(100), 346(3.1), 345(0.2), 333(0.3), 329(0.1), 317(0.3), 301(0.4), 287(0.8), 276(0.2), 275(1.6), 257(0.3), 248(0.6), 247(3.7), 246(0.1), 231(0.2), 230(0.5), 229(3.6), 228(0.3), 101(1.2). $W_{Q^+} = 88\%$.

In the CI mass spectra of compounds (I-X), the peaks of maximum intensity are those of the quasimolecular ions $Q^+ = (M + H)^+$. The ions $Q_1^+ = (M + C_2H_5)^+$ and $Q_2^+ = (M + C_3H_5)^+$ are also observed, and in the case of compounds (III-V and VII), in addition, the ions $Q_3^+ = (M + CH_3)^+$ are present with considerably lower intensity. The stabilities of the ions Q^+ (W_{Q^+}) *, calculated in a similar manner to the stability of the ions $M^{+\bullet}$(W_{M^+}), in electron-impact mass spectra [5] are 43-92%, while on CI they are 1.5-8.0%.

For the hydroxydihydropyranocoumarins, the values of W_{Q^+} for the linear and angular isomers (I, II) are approximately the same, while in the case of the hydroxydihydrofurocoumarins (V, VI) the value is far higher for the linear isomer (V). For acyl derivatives, the values of W_{Q^+} are greater for the dihydropyranocoumarins than for the dihydrofurocoumarins isomeric with them. In the mass spectra of the angular acyloxydihydropyranocoumarins and dihydrofurocoumarins the stability of the ion Q^+ is 1.3-1.4 times greater than for their linear isomers.

Under the conditions of chemical ionization, unlike those of electron impact, the hydroxy derivatives of the dihydropyranocoumarins and dihydrofurocoumarins (I, II, V, VI) split off mainly a molecule of H_2O, giving, like the acyl derivatives, the ion $(Q - ROH)^+$ with m/e 229, where R = H, Ac (Scheme 1).

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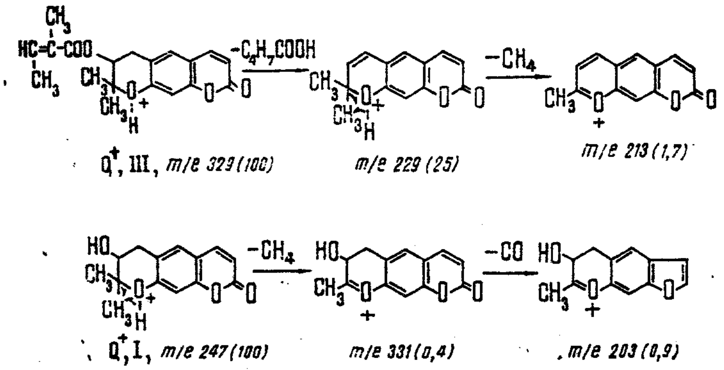
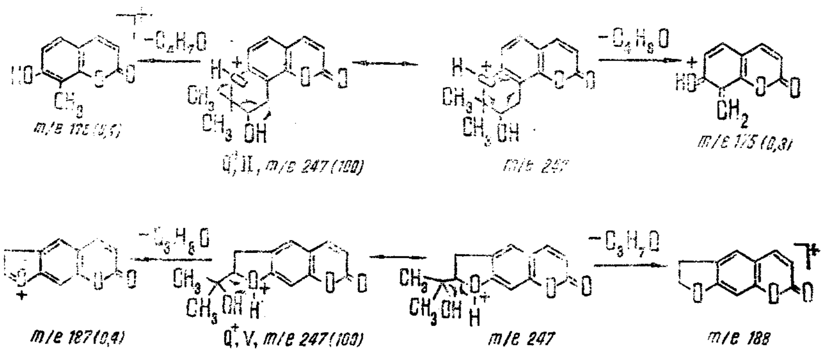
*In calculating W_{Q^+} the contributions of the ions Q_1^+, Q_2^+, and Q_3^+ and the fragments formed from them were excluded from the total ion current.



Scheme 1

An exception is formed by the fragmentation of agasyllol (I), in which the cleavage of the dihydropyran ring with the formation of ions having m/e 176 and 175 takes place with a probability approximately 1.5 times greater than the elimination of an H_2O molecule. In the mass spectra of the angular hydroxy derivative (II) and (VI), the intensity of the fragment $(Q - H_2O)^{+\cdot}$ is 2.5–4 times greater than for their linear isomers (I) and (VI). In the case of the acyl derivatives, conversely, the spectra of the linear isomers contain a more intense $(Q - ROH)^{+\cdot}$ fragment with m/e 229: in the mass spectrum of the linear linked compound (III) the intensity of the ion with m/e 229 is 6.7 times higher than for the angular isomer (IV), and in the case of the linear acyloxydihydrofurocoumarin (VIII) the intensity of this ion is 1.2 times higher than that of its angular isomer (IX). Furthemore, for the dihydrofurocoumarins (V-X) the formation of the fragment $(Q - ROH)^{+\cdot}$ takes place with a considerably greater probability (approximately three times and more) than for the dihydropyranocoumarins isomeric with them. In the mass spectra of (I-X), the loss of a ROH molecule (R = H, Ac) is also observed in the decomposition of the ions $Q_1^+ = (M + C_2H_5)^+$. However, the intensities of the fragments $(Q_1 - ROH)^{+\cdot}$ formed are not in harmony with the rules mentioned above for the intensity of the $(Q - ROH)^{+\cdot}$ fragments with the exception of the fact that the linear acyloxy derivative (III and VIII) give a larger peak of the ion $(Q_1 - AcOH)^{+\cdot}$ than their angular isomers (IV and IX). The latter also show a smaller number of daughter fragments $(Q_1 - AcOH)^{+\cdot}$ with m/e 257, $(Q_2 - AcOH)^{+\cdot}$ with m/e 269, $[Q_1 - (Ac - H)]^+$ with m/e 275, and $[Q_2 - (Ac - H)]^+$ with m/e 287 as compared with the linear compounds (III, VII, VIII, and X). This rule also applies to the mass spectra of the hydroxy derivatives of the dihydropyranocoumarins (I and II), while in the case of the decomposition of the hydroxydihydrofurocoumarins (V and VI) isomeric with them a larger number of these ions is observed in the mass spectrum of the angular isomer (VI). The elimination of a ketene molecule by the quasimolecular ion Q^+ of the acyl derivative (III, IV, VII-X) leads to the formation of the fragments $[Q - (Ac - H)]^+$ with m/e 247 having a greater intensity in the case of compounds of the linear type.

Fragments with m/e 176 and 175 formed by the cleavage of the dihydropyran or dihydrofuran ring of one of compounds (I-X) on electron impact are observed in the CI mass spectra only for the hydroxydihydropyranocoumarins (I and II). Their appearance, like that of the ions with m/e 188 and 187 in the CI mass spectra of the hydroxydihydrofurocoumarins (V and VI), and also of the fragment with m/e 213 in the case of the acyl derivatives (III, IV, VII, and VIII), is readily explained by the fragmentation of the $M^{+\cdot}$ ions arising together with the quasimolecular ions Q^+ under the conditions of the chemical ionization of (I-X). This hypothesis is based on the fact that these fragments have the maximum intensities in the CI mass spectra of the corresponding compounds, while in the CI mass spectra, with the exception of (I), they do not undergo shifts by 1 amu in the direction of higher masses. At the same time, the ions with m/e 231 and 203 having a low intensity on electron impact and, consequently, being formed only through the fragmentation of the ion Q^+ under the conditions of chemical ionization, do not show a shift by 1 amu in the CI mass spectra of substances (I, II, and V). The appearance of these ions can be explained by the protonation of the oxygen of the dihydropyran and dihydrofuran rings of the molecules of (I, II, and V) followed by the elimination of the neutral particles CH_4 and CO (see Scheme 1).



Scheme 2

This hypothesis permits an explanation of the appearance of fragments with m/e 176, 175 and 188, 187, from the ion Q^+ of compounds (II) and (V, VI), respectively (Scheme 2) and also of the fragment with m/e 213 in the decomposition of the Q^+ ion of the acyl derivatives (III, IV, VII, and VIII) (see Scheme 1). The displacement of the peak of the fragment with m/e 176 in the CI mass spectrum of substance (I) by 1 amu confirms the possibility of the cleavage of the dihydropyran ring under the conditions of the chemical ionization of the compounds (I and II) and shows that the protonation of their molecules apparently takes place not only at the oxygen atom of this ring. The formation of a fragment with m/e 187 in the CI mass spectra of (I) and (II), this fragment having a low intensity on electron impact, can be explained by the rearrangement of the Q^+ ions of compounds (I and II) into the quasimolecular ions of substances (V and VI) isomeric with them. The absence of a fragment with m/e 188 in the CI mass spectra of (I) and (II), in contrast to the mass spectra of (V and VI) indirectly confirms the fragmentary nature of this ion under the conditions of the chemical ionization of the hydroxydihydrofurocoumarins (V) and (VI) (see Scheme 2), since the rearrangement of the Q^+ ions of substances (I) and (II) as a result of which the fragment with m/e 187 is formed reduces their store of internal energy as compared with the quasimolecular ions (V) and (VI).

The CI mass spectra of the acyl derivatives (III, IV, and VII-X) contain the fragment $RC\equiv\overset{+}{O}$, as in the case of the electron impact fragmentation of these substances. The linear isomers (III and VIII) give a more intensive peak of the $RC\equiv\overset{+}{O}$ than the angular isomers (IV and IX). In addition to common features, some of compounds (I-X) show specific fragmentation characteristics under the conditions of chemical ionization. Thus, the mass spectra of substances (I, VI, and VIII) show the formation of the fragment $(Q - ROH - C_3H_8)^+$ with m/e 215, and the mass spectra of compounds (III and VI) show the formation of the ions $(Q_3 - CO)^+$ with m/e 317 and $[Q_1 - (CH_3)_2CO]^+$ with m/e 217, respectively. Compound (X) gives the fragment $(Q - SCH_2)^+$ with m/e 301, which is not formed in the electron impact of (X).

Thus, in spite of the substantially smaller number of fragmentary ions and their very low intensity in comparison with electron impact, the chemical ionization mass spectra of the monohydroxy- and monoacyloxy-substituted dihydropyranocoumarins and dihydrofuranocoumarins make it possible to distinguish hydroxy from acyloxy derivatives, linear isomers from angular, and dihydropyranocoumarins from dihydrofurocoumarins. The maximum intensity of the quasimolecular ions permits the molecular weights of this group of compounds to be established more reliably, enables the molecular ions to be identified when mixture are being studied, and considerably (by a factor of 5-8) increases the sensitivity of the method in the detection of small amounts of the substances under investigation.

EXPERIMENTAL

The chemical ionization mass spectra of compounds (I-X) were obtained on a Finnigan 3200-F quadrupole mass spectrometer with the direct introduction of the samples into the ion source. Methane at a pressure of 0.5 mm Hg was used as the reagent gas. The energy of the ionizing electrons was 140 eV, the temperature of evaporation of the sample 120-200°C, and the temperature of the ionization chamber ~ 125°C.

SUMMARY

The chemical ionization mass spectra of ten compounds of the group of natural monohydroxy and monoacyloxy derivatives of dihydropyranocoumarins and dihydrofurocoumarins have been studied. Their difference from the electron impact mass spectra has been shown. The structural-analytical possibilities of the method of chemical ionization for this series of substances has been determined.

LITERATURE CITED

1. M. Shipchandler and T. O. Soine, J. Pharm. Sci., 57, 2062 (1968).
2. M. Shipchandler and T. O. Soine, J. Pharm. Sci., 57, 741 (1968).
3. P. I. Zakharov, P. B. Terent'ev, G. K. Nikonov, and A. I. Ban'kovskii, Khim. Prirodn. Soedin., 431 (1972).
4. P. I. Zakharov, V. S. Kabanov, A. I. Bankovskii, G. K. Nikonov, and N. E. Ermatov, Khim. Prirodn. Soedin., 398 (1971).
5. A. Paal, Z. Naturforsch., 96, 418 (1954).

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^{13}C NMR SPECTRA OF 3- AND 5-SUBSTITUTED FLAVONE DERIVATIVES

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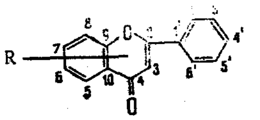
In a study of the acid–base characteristics of flavone compounds [1-3] a number of features of the behavior of compounds with the 3- and 5- models of substitution have been detected the reason for which consists in the specific natures of their electronic and geometrical structures [4, 5].

In view of the fact that changes in the ^{13}C chemical shifts agree semiquantitatively with changes in the electron densities on the corresponding carbon atoms under the influence of substituents in an aromatic system [6, 7], we have studied the ^{13}C NMR spectra of the compounds of interest to us in order to obtain information on their electronic structures.

In the present work we have considered the ^{13}C spectra of 3-hydroxyflavone (II), 3-methoxyflavone (III), 5-hydroxyflavone (IV), and 5-methoxyflavone (V) and have identified all the signals (Table 1)



I. $R = H$
II. $R = 3\text{-OH}$
III. $R = 3\text{-OCH}_3$
IV. $R = 5\text{-OH}$
V. $R = 5\text{-OCH}_3$

The assignment of the signals was based on the results obtained both from high-resolution ^{13}C NMR spectra and from spectra with the broad-band suppression of spin–spin coupling with ^{1}H nuclei.

The procedure for the interpretation of the spectra has been explained for, as an example, the case of 3-hydroxyflavone, the ^{13}C NMR spectrum of which is shown in Fig. 1. Under the conditions of broad-band decoupling from the protons, the signals corresponding to the pairs of equivalent carbon atoms C-2', 6', and C-3', 5' of the aromatic ring B (127.63 and 128.46 ppm) are distinguished from the signals of the other ^{13}C nuclei having directly attached protons by their approximately doubled intensity. Their relative assignment is simple, since the $^{13}C-{}^1H$ constants through three bonds in the benzene ring are always considerably greater in absolute magnitude than through two or four bonds [10] and have values of the order of 6-10 Hz. The signal with δ 127.63 ppm appears in the high-resolution spectrum as a doublet of triplets ($^1J_{CH}$ 163.2 Hz; $^3J_{CH}$ 6.6 Hz), i.e., it can be assigned to the C-2',6' atoms, each of which has two protons attached to the meta carbon atoms (C-4',6' and C-2',4', respectively).

The signal with δ 128.46 ppm is a doublet of doublets ($^1J_{CH}$ 162.1 Hz, $^3J_{CH}$ 6.2 Hz) with a small additional splitting of the components, i.e., it corresponds to the C-3',5' carbon atoms. In the high-resolu-

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Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. A. A. Zhdanov Irkutsk State University. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 513-519, July-August, 1977. Original article submitted February 24, 1977.