2. It has been established by enzymatic hydrolysis with phospholipase A_2 of kufi venom that the unsaturated fatty acids are present in position of the PCh, PE, and PI molecules – to the extent of 90.6%, 96.5%, and 85.4%, respectively.

3. From the position distribution of the fatty acids in the phospholipids, their possible molecular compositions have been calculated.

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THE DEPENDENCE OF THE FATTY-ACID COMPOSITION OF COTTONSEED OIL ON THE DEGREE OF UNSATURATION

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The dependence investigated is of considerable interest from the practical point of view. Any strict determination of it would provide fat chemists and merchants with the possibility of quantitatively evaluating the composition of an oil from such a readily available index as the iodine number.

Furthermore, the problem is also of interest for the chemistry of natural compounds and products, particularly from the point of view of Academician S. L. Ivanov's climatic theory of the formation of organic substances [1].

The quality of cottonseed oil is determined primarily, if there are no technological peculiarities in its production, by the ratio of linoleic and oleic acids; this to a certain extent determines the composition and properties of the products of its reduction, and also the conditions of the actual catalytic hydrogenation process. Consequently, in this case it is precisely the dependence of the amount of each of these two unsaturated acids on the degree of unsaturation that is important, while the quantitative differentiation of the acyl radicals has no such importance.

At the present time, various authors have obtained two pairs of equations by which attempts have been made to express the required relationship.

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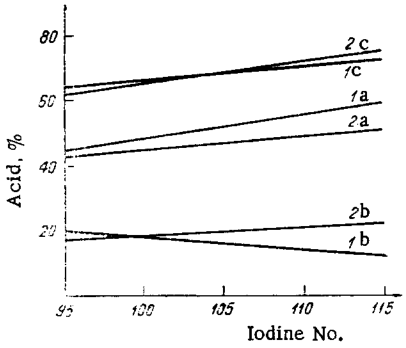

Fig. 1. Dependence of the amount of linoleic acid (1a and 2a) and oleic acid (1b and 2b) and of their sum (1c and 2c) on the iodine number according to Eqs. (1) and (2), and (3) and (4).

A. Bailey et al. [2], having treated their own results of the chromatographic analysis (GLC) of 22 samples of cottonseed oil statistically by the method of least squares, found the following pair of equations of the type of $Y = \pm KX \pm b$:

$$L = 0.7882\ \text{I. No.} - 30.84, \quad (1)$$

$$Ol = -0.3625\ \text{I. No.} + 55.54 \quad (2)$$

for linoleic and oleic acids, respectively.

According to Eqs. (1) and (2) with an increase in the degree of unsaturation of the oil the amount of linoleic acid in it rises (Fig. 1, curve 1a), and the amount of oleic acid falls almost in proportion (curve 1b). However, as the authors mentioned observed, the total of the enoic acids (curve 1c) rises from sample to sample only very slightly (the amount of palmitoleic acid is not taken into account in Fig. 1).

It has been shown [3-5] that in the catalytic hydrogenation of cottonseed oil using potentiometric monitoring of the state of the catalyst a simpler relationship is found, of the type of $Y = KX$:

$$L = 0.4515\ \text{I. No.} \quad (3)$$

$$Ol = 0.2026\ \text{I. No.} \quad (4)$$

where the symbol Ol denotes the total amount of monoenoic acids.

As shown in Fig. 1, according to Eqs. (3) and (4) with a rise in the iodine number the amount of linoleic acid (curve 2a) should increase and that of oleic acid somewhat less markedly (curve 2b). Naturally, in this case the total amount of unsaturated acids (curve 2c) rises faster than according to Bailey.

We have treated the results given in the literature [3-5] statistically by the method of least squares in confirmation of Eqs. (3) and (4), and this has given equations extremely similar to the latter:

$$L = 0.4580\ \text{I. No.} \quad (5)$$

$$Ol = 0.2032\ \text{I. No.} \quad (6)$$

When, however, in this treatment the results of the chromatographic analysis were excluded, the results proved to be even closer to Eq. (3) and (4):

$$L = 0.4525\ \text{I. No.} \quad (7)$$

$$Ol = 0.2003\ \text{I. No.} \quad (8)$$

The successive exclusion of the results of other methods (thiocyanometry and spectrophotometry) led to the opposite effect. Subsequently, it was observed that the results of chromatographic analysis actually correspond to a smaller degree than the others to the relationship found potentiometrically. This unavoidably faced us with the problem of the separate statistical treatment of the largest possible number of results obtained by chromatographic analysis and (in counterbalance to the latter) by other methods.

We have also treated statistically by the method of least squares the results of a quantitative (for acids) analysis of 72 samples of cottonseed oil given in the literature during the last few years. The results of the thiocyanometry and spectrophotometry of 39 samples gave the relations

$$L=0,4514\ \text{I. No.} \tag{9}$$

$$\text{Ol}=0.2180\ \text{I. No.} \tag{10}$$

which, as can be seen, practically coincide with those found potentiometrically.

Analyzing the remaining 33 samples (chromatographic method), we obtained the equations

$$L=0,578\ \text{I. No.}-8,88, \tag{11}$$

$$\text{Ol}=-0,309\ \text{I. No.}+49,97, \tag{12}$$

extremely close, particularly Eq. (12), to those obtained by Bailey, et al.

Thus, for cottonseed oil a tendency has been found for the chromatographic method to differ from a number of other methods – spectrophotometry, thiocyanonometry, and potentiometry. The statistical treatment of analogous results for sunflowerseed oil which we are performing at the present time will apparently permit an investigation of the width of this tendency.

We can consider the equation of the Y = KX type

$$L=0,4932\ \text{I. No.} \tag{13}$$

which we obtained for the same 22 samples [2] as an indirect argument in counterbalance to Eqs. (1) and (2). For this, the sum of the squares of the deviations is only slightly greater than for (1): 24.01 and 20.74. In view of the comparatively small number of samples, the latter fact will hardly permit us to prefer to Eq. (1) definitely over Eq. (13). However, on substituting the value of L from (13) in the well-known balance equation 1.81 L + 0.899 Ol = I. No. for oleic acid we obtain

$$\text{Ol}=0,118\ \text{I. No.} \tag{14}$$

where its amount also rises with an increase in the degree of unsaturation.

Finally, the idea of the competing accumulation of linoleic acid at the expense of oleic also finds some objection on the part of phytochemists. In L. S. Ivanov's opinion [1], the biosynthesis of linoleic acid begins at a later stage of vegetation than that of oleic acid and its accumulation cannot take place at the expense of the latter. In the general case, the realization of Bailey's equations can take place only with antibatically conjugated climatic conditions of two adjacent vegetation phases, i.e., the more unfavorable the climate at the beginning of the ripening of the seeds, the more favorable must it be at the end of this process. As we see, the premise clearly contradicts the real conditions.

It is known that the iodine number is not a quantitatively strict and sufficiently universal index of the degree of unsaturation of natural oils. It would be more logical to use a more objective index – the unsaturation number [7]. However, since in this case the question of the existence of the required dependence and its nature is solved, the iodine number fully satisfies this task as an index of unsaturation.

SUMMARY

1. Results of thiocyanometric and spectrophotometric analysis of cottonseed oil confirm the relationship found previously in catalytic hydrogenation using potentiometric monitoring of the state of the catalyst.

2. Together with Eqs. (3) and (4), these results counterbalance the results of the chromatographic analysis of cottonseed oil.

3. This contradiction leads to the posing of the question of the probable inaccuracy of individual methods of chromatographic analysis for substances with similar absorption properties, i.e., for linoleic and oleic acids.

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THE STRUCTURE OF KARATAVIC ACID

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Continuing an investigation of the structure of karatavic acid [1], we have made a detailed study of the NMR spectra of the methyl ester of this acid and also of the products of the alkaline hydrolysis of its ethyl ester. The results obtained show that the structure proposed previously for karatavic acid requires reconsideration.

In the NMR spectrum of the methyl ester of this acid (Fig. 1, curve 1), there are the signals of a tertiary methyl group (0.87 ppm), of two methyl groups on double bonds (1.65 and 1.76 ppm), and of an ester methyl group (3.52 ppm). In the 3.57-4.20 ppm region there are the signals characteristic for the $Ar-O-CH_2-CH <$ grouping in terpenoid coumarins [2-13].

The signals of the protons of the methyl group at 1.76 ppm and of the olefinic protons (4.73 and 4.81 ppm) relate to an isopropenyl grouping [14], as was shown by double resonance (Fig. 1, curve 2). On irradiation (strong field H_2) of the signal of the methyl group (1.76 ppm), the signals at 4.73 and 4.81 ppm contracted and were converted into two doublets ($^2J = 1.9$ Hz). The signal of the olefinic proton of a $H-C=C-CH_3$ fragment also contracted, also contracted, which shows the close positions of the double bonds.

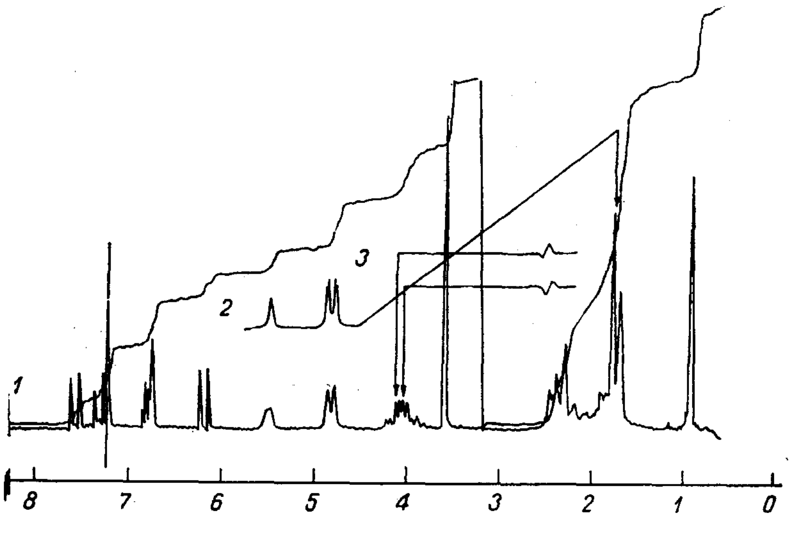

Fig. 1. NMR spectrum of methyl karatavate (1), double resonance (2), INDOR (3) ($CDCl_3$, 100 MHz, 0, δ, ppm, HMDS).

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