TRANSESTERIFICATION OF MIXTURES OF TRIGLYCERIDES IN THE PRESENCE OF COTTON-PLANT LIPASE

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The transesterification of mixtures of cottonseed oil with beef fat in the presence of cotton plant lipase immobilized on a solid support has been studied. A regime for the transesterification of the triglycerides permitting transesterificates suitable for the production of margarine and bakers' and confectioners' articles have been found.

An improvement in the process of the catalytic transesterification of mixtures of triglycerides requires the choice of a new more effective transesterification catalyst of the acid residues of the triglycerides present in the "system" which will permit an increase in the productivity of the process and an improvement in the quality of the transesterificate. At the present time, preference in this direction is being given to biocatalysts for the transesterification of triglycerides, since their use increases the yield of transesterificate and improves its quality.

The well-known alkali-metal [1] and alkaline-earth-metal [2] alcoholates frequently saponify the neutral fat present in the mixture being transesterified and, consequently, lower the yield and quality of the transesterificate obtained.

The aim of the present investigation was to evaluate the influence of individual factors on the process of the redistribution of acid residues of mixtures of plant oils and animal fats on biocatalysts.

As the biocatalyst we used lipase obtained from cotton seeds and immobilized on a solid support [3].

The initial reagents for the mixture to be transesterified were: refined cottonseed oil with an iodine number of 110.1 I_2% and an acid No. of 0.01‰, and beef fat with a hardness of 340 g/cm (according to Kaminskii) having mp 42.1°C with an acid number of 2.3‰. The quantitative ratio of the reagents in the mixture was kept constant — 1:1.

In view of the fact that the hydrolytic function of cottonseed lipase is exhibited in the range of pH values of the medium of 4.0-6.0, we considered the influence of the pH of the medium on the process of transesterifying a mixture of cottonseed oil and beef fat (H — hardness; A — lipase activity):

pH of the medium	mp, °C	H, g/cm	A, %	Content of solid glycerides, %			
				20°	30°	35°	40°
5.0	42.4	296	0	323	17.4	13.2	12.1
5.5	39.8	272	10	21.2	14.2	8.8	5.8
6.0	39.2	264	22	18.8	11.2	9.1	6.2
6.5	38.4	246	50	18.9	9.7	6.4	5.2
7.0	38.0	232	62	17.2	9.8	7.4	6.1
7.5	36.0	224	74	18.4	10.2	7.6	5.8
8.0	36.1	238	72	19.8	11.2	9.1	6.2
8.5	36.2	240	74	17.4	9.4	7.6	5.8

As we see, with a rise in the pH of the medium the melting point and hardness of the transesterificates fell sharply, which is due to the physicochemical properties of the product obtained. Consequently, to ensure the efficacy of the transesterification process and to obtain a product with the desired physicochemical indices the pH of the medium must be kept between 7.5 and 8.5.

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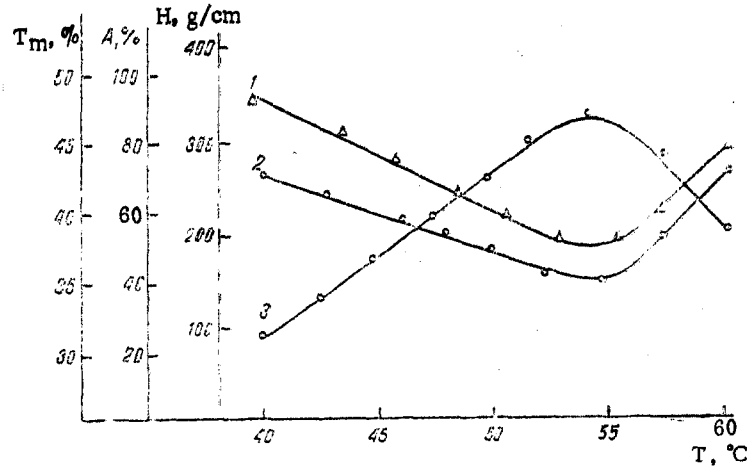

Fig. 1. Dependence of the hardness and melting point of the transesterificate and the activity of the process on the temperature of transesterification: 1) curve of the hardness of the transesterificate; 2) melting point of the transesterificate; 3) activity of the transesterification process.

The efficacy of the enzymatic transesterification of triglycerides depends to a considerable degree on the temperature conditions. This factor was studied at 45-60°C. Figure 1 shows the results of a study of the dependence of the change in the physicochemical indices of the desired product on the temperature conditions of the transesterification process. At low temperatures, the enzyme preparation is incapable of changing the glyceride structure of the mixture of fats.

The optimum temperature may be considered to be 50-55°C. A further rise in the temperature does not give a favorable effect, since the lipase begins to lose its activity.

We studied the influence of the amount of proposed biocatalyst on the transesterification of triglycerides. The amount of cottonseed lipase in the mixture being transesterified substantially affects the melting point and hardness of the transesterificate up to an amount of added biocatalyst of 0.40%. A further increase in the amount of biocatalyst has a very slight effect on the transesterification of the acid residues of the triglycerides present in the mixture undergoing transesterification:

Amount of catalyst, %	mp, °C	H, g/cm	Content of solid triglycerides, %			
			20°	30°	40°	50°
0.13	39.2	162	21.2	14.3	9.2	3.4
0.15	38.4	158	19.8	14.2	10.4	4.1
0.20	37.5	149	18.4	16.2	9.1	5.4
0.40	36.4	140	17.2	9.8	7.4	3.1
0.50	36.2	140	17.4	8.4	5.4	3.2

Thus, by using a biocatalyst, i.e., cottonseed lipase, the transesterification of the fatty acid radicals of triglycerides can be carried out at a fairly high rate. At the same time, the rate of redistribution of the fatty acid radicals will depend on the conditions of the transesterification process.

EXPERIMENTAL

The experiments were carried out in a laboratory transesterifying reactor fitted with an electrically driven stirrer, necks for the addition of the reagents, a thermometer, and a heating device. For the transesterification of a mixture of cottonseed oil and beef fat we used cottonseed lipase immobilized on a solid support [3]. The transesterification of the mixtures of triglycerides was studied at 40-60°C, a pH of the medium of 5.0-8.5, and with an amount of biocatalyst varying from 0.13 to 0.50% of the weight of the transesterification mixture.

SUMMARY

It has been established that by using cottonseed lipase it is possible to effect the transesterification of the fatty acid radicals of mixtures of triglycerides. The transesterificates so obtained correspond completely in their structural and mechanical properties to the demands set for the fatty bases used for the production of margarine and bakers' and confectioners' articles.

LITERATURE CITED

1. T. T. Mirkhalikov, A. Abdurakhimov, and P. A. Artamonov, Khim. Prir. Soedin., 13 (1973).
2. A. G. Sergeev, N. L. Melamud, and R. L. Perkel', The Production of Transesterified Food Fats for the Manufacture of Margarine [in Russian], Moscow (1973).
3. A. A. Virnik, R. I. Fesenko, Yu. V. Artemova, and Z. A. Rogovin, in: Abstracts of Lectures at the 1st All-Union Symposium on the Production and Use of Immobilized Enzymes [in Russian], Tallin (1974), p. 85.

^1H AND ^{13}C NMR SPECTRA AND THE STRUCTURE OF A NEW COUMARIN, C-GLYCOSIDE DAUROSIDE D, FROM *Haplophyllum dauricum*

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On the basis of chemical transformations, ^1H and ^{13}C NMR spectra, the structure of dauroside D isolated from *Haplophyllum dauricum* has been established as 6-C-β-D-glucopyranosyl-5,7-dihydroxycoumarin. Some interesting features of the ^1H NMR spectra of its acetate have been reported and an assignment of the signals in its ^1H and ^{13}C NMR spectra has been made. Dauroside D is the first natural coumarin C-glycoside.

Previously [1] on the basis of its chemical and spectral characteristics, a structure was proposed for dauroside D isolated from *Haplophyllum dauricum* (L.) G. Don in which the position of the carbohydrate residue was not established unambiguously. For a definitive solution of this problem we have used the method of double resonance in the PMR spectrum of dauroside D (I) and its acetyl derivative, and we have also studied the ^{13}C NMR spectrum of (I).

The PMR spectrum of dauroside D taken at room temperature in DMSO-d_6 (Fig. 1) shows the following signals: at 6.00 and 7.92 ppm, one-proton doublets with J = 10 Hz relating to the H_3 and H_4 protons of the coumarin nucleus, respectively, the components of the H_4 doublet being somewhat wider than those of the H_3 doublet; at 6.25 ppm, a broadened one-proton doublet belonging to one of the aromatic protons of the coumarin skeleton. At 4.70 ppm, a doublet from the H_1' protons of the sugar moiety partially overlapping with the signal from hydroxylic protons with its center at 4.95 ppm. In the 2.95-3.85 ppm region appear signals from the H_2'-H_6' protons of the sugar residue — β-D-glucose. The cleavage of (I) with Kiliani's mixture yielded 5,7-dihydroxycoumarin [1]. Consequently, the phenolic OH groups in dauroside D are located at C_5 and C_7, and the broadened singlet at 6.25 ppm can relate only to H_6 or H_8. The determination of the position of the sugar residue in the coumarin nucleus of (I) reduced to the unambiguous assignment of the signal with δ 6.25 ppm to H_6 or H_8.

This problem was solved with the aid of double proton resonance. As can be seen from Fig. 1, and as mentioned above, the signal of the H_4 proton is somewhat broadened in comparison with the signal from the H_3 proton. It is known [2, 3] that the long-range SSCC of H_4 with H_8 in coumarin systems is $^5J_{4,8} \approx 0.6$-0.7 Hz, while $^5J_{4,6} \approx 0$.

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