gel in the hexane—ethyl acetate system. This gave a crystalline substance with the composition $C_{10}H_{10}O_4$, M^+ 194, mp 174-175°C, which was identified as ferulic acid [1-4]. The iridoids were obtained by extraction with n-butanol from the concentrated methanolic extract of the *Ziziphora* after its treatment with ether [2, 5]. The extract contained a mixture of three substances with R_f 0.27, 0.45, and 0.68 [Silufol, chloroform—methanol (4:1); visualization with the Stahl reagent]. The solution was passed through alumina and was chromatographed on a column of silica gel. Washing with chloroform—methanol yielded an amorphous hygroscopic substance with the composition $C_{16}H_{20}O_{10}$, R_f 0.45, that, on the basis of qualitative reactions and absorption maxima in the UV spectrum at 206 and 227 nm, which are characteristic for a conjugated carbonyl group, was assigned to the iridoids [5, 6].

The aglycon could not be isolated by acid hydrolysis since it resinified, but in the sugar fraction of the hydrolysate D-glucose was detected by PC in the butan-1-ol—acetic acid—water (4:1:2) system in the presence of a marker. Thus, caffeic and ferulic acids and an iridoid with the composition $C_{10}H_{20}O_{10}$ have been isolated from a *Ziziphora* for the first time.

LITERATURE CITED

1. V. A. Bandyukova, Khim. Prir. Soedin., 263 (1983).
2. N. F. Komissarenko, A. I. Derkach, I. P. Sheremet, and D. A. Pakali, Khim. Prir. Soedin., 109 (1976).
3. F. A. Rasulov, A. Sh. Ibragimov, and M. B. Belyi, Khim. Prir. Soedin., 524 (1983).
4. N. V. Sergeeva, V. A. Bandyukova, D. K. Shapiro, T. I. Narizhnaya, and L. V. Anikhimovskaya. Khim. Prir. Soedin., 726 (1980).
5. C. H. Brieskorn and R. Ahlborn, Tetrahedron Lett., No. 41, 4037 (1973).
6. K. Weinges, P. Kloss, and W. D. Henkels, Ann. Chem., 767, 4 (1973), p. 556.

BITTER IRIDOID GLUCOSIDE FROM THE FRUIT OF Lonicera caerulea

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547.477.1

The fruit of sweetberry honeysuckle is used in folk medicine as a hypotensive agent in hypertonic disease. The use of the berries as a food product is limited by their specific bitter taste.

The material for investigation was collected in July, 1986, in Sverdlovsk province. To determine the chemical nature of the bitter components of the fruit of *Lonicera caerulea* L. (sweetberry honeysuckle), family Caprifoliaceae, aqueous ethanolic extracts were fractionated successively with hexane, chloroform, ether, and ethyl acetate. It was found that the bitterness of the fruit was due to a complex of minor components which were detected in various fractions of the extract.

When the water-soluble residue from the extract of fresh fruit was chromatographed on polyamide with elution by water, a bitter fraction of substances which included citric acid was obtained. The fraction was methylated with diazomethane and was chromatographed on a column of silica gel. The main component, trimethyl citrate [1], mp 77-78°C, was eluted by chloroform and by chloroform—methanol (200:1). When the proportion of methanol was increased to 10%, a bitter iridoid glycoside was eluted that was identified as 7-oxologanin (I) on the basis of the facts given below.

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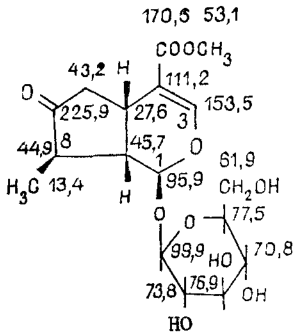

Compound (I), $C_{17}H_{24}O_{10}$, $(M + H)^+$, m/z 389 (FAB mass spectrometry), mp 194-195°C (isopropanol), $[\alpha]_{546}^{20}$ −161.3°(c 1.19; H_2O); $\lambda_{max}^{CH_3OH}$ 234 nm, ν_{max}^{KBr} 1740, 1680, 1640, 3100-3600 cm^{-1}. PMR spectrum (CD_3OD; δ, ppm: HMDS): 1.15 d (3H, J = 6 Hz, CH_3), 3.68 s (3H, OCH_3), 5.62 d (1H, J = 3 Hz, H-1), 7.49 d (1H, J = 1.22 Hz, H-3) [2].

The assignment of the signals in the ^{13}C NMR spectrum of (I) taken in D_2O (with dioxane as internal standard) was made by comparison with those for loganin and verbenalin [3].

Compound (I) could be formed from the corresponding acid by methylation with diazomethane. The native nature of (I) was confirmed by its isolation from the initial unmethylated fraction after the elimination of citric acid from it with the use of AV-17 ion-exchange resin. The isolation of 7-oxologanin from plants of the genus Lonicera has not been reported previously.

LITERATURE CITED

1. A. Loewenstein and J. D. Roberts, J. Am. Chem. Soc., 82, 2705 (1960).
2. V. A. Mnatsakanyan, Iridoid Glycosides [in Russian], Izd. AN ArmSSR, Erevan (1986).
3. C. J. Coscia, R. Guarnaccia, and L. Botta, Biochemistry, 8, No. 12, 5036 (1969).

CITRIC ACID ESTERS FROM FRUIT OF Lonicera caerulea

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Continuing a study of the fruit of Lonicera caerulea L. [1], we have chromatographed on ethyl acetate extract on silica gel and have obtained three fractions: A) by elution with chloroform; B, C) by elution with chloroform—methanol (19:1).

By crystallization from water, fraction C yielded compound (I), $C_8H_{12}O_7$, mp 91-92°C (H_2O), FAB MS $(M + H)^+$, m/z 221, $[\alpha]_{546}^{20}$ 0° (c 1.32, CH_3OH), identified as sym-dimethyl citrate [2].

Rechromatography of fraction A on a column of silica gel in hexane and hexane—acetone (17:3) led to the isolation of syn-di-n-butyl citrate (II), $C_{14}H_{24}O_7$, FAB MS, $(M + H)^+$, m/z 305, n_D^{20} 1.4628, $[\alpha]_{546}^{20}$ 0° (c 1.85; H_2O).

In the same way, by using benzene and benzene—acetone (9:1) as solvents, fraction B yielded the liquid 1-n-butyl citrate (III), $C_{10}H_{16}O_7$, $(M + H)^+$, m/z 249, n_D^{20} 1.4245, $[\alpha]_{546}^{20}$ −2.14° (c 1.82; CH_3OH). From compound (III), by methylation with diazomethane, an ester (IV) was obtained with the composition $C_{12}H_{20}O_7$, $(M + H)^+$, m/z 277, n_D^{20} 1.4472.

The structures of substances (I-III) were determined on the basis of an analysis of their IR and ^1H and ^{13}C NMR spectra and by mass-spectrometric fragmentation. These com-

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