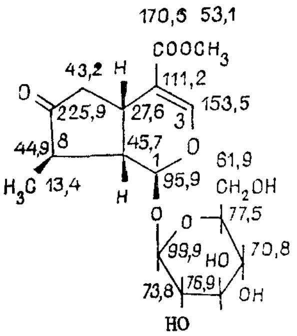

Compound (I), $C_{17}H_{24}O_{10}$, $(M + H)^+$, m/z 389 (FAB mass spectrometry), mp 194-195°C (isopropanol), $[\alpha]^{20}_{546}$ −161.3°(c 1.19; H_2O); $\lambda_{max}^{CH_3OH}$ 234 nm, ν_{max}^{KBr} 1740, 1680, 1640, 3100-3600 cm^{-1}. PMR spectrum (CD_3OD; δ, ppm: HMDS): 1.15 d (3H, J = 6 Hz, CH_3),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

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CITRIC ACID ESTERS FROM FRUIT OF Lonicera caerulea

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581.47

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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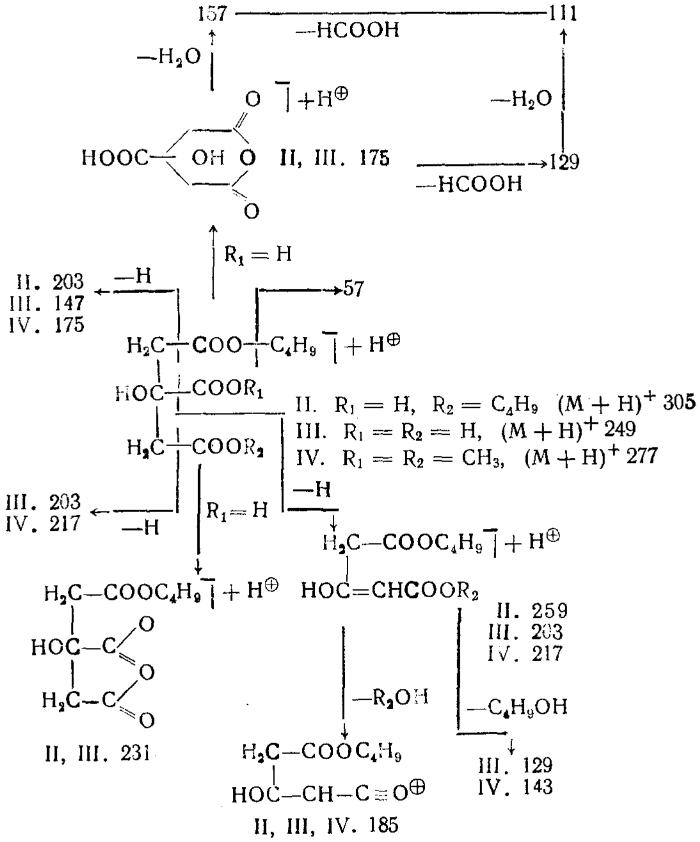
pounds do not give the molecular ions on ionization by electron impact. The use of the FAB (fast-atom bombardment) method enabled both the value of the molecular weight and also the pattern of fragmentation (scheme) to be obtained, which confirmed their chemical structures. For compounds (II-IV), a tendency to the formation of clusters containing up to three or four molecules was observed. The FAB mass spectra were taken without a matrix on an LKB-2091 spectrometer with ionization by Xe atoms having an energy of 6 keV at a discharge current of 1 mA.



We have found no reports of the presence of butyl esters in plant materials. Dimethyl citrate has been found in the fruit of Ananas sativus and Crataegus [4, 3].

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