THE STRUCTURE OF ALGINOSIDE, A γ-LACTONE OF Rhodiola algida

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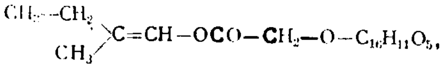
From the epigeal part of Rodiola algida (Ledeb). Fisch et Mey, family Crassulaceae, collected in the flowering phase in the north-western Altai we have isolated a new colorless crystalline substance with mp 192° C, composition $C_{13}H_{22}O_8$, which we have called algidin (I).

The acid and enzymatic hydrolysis of (I) with β-glucosidase split off D-glucose and gave an aglycone with the composition $C_7H_{12}O_3$. The PMR spectrum of the tetraacetate of (I) (Fig. 1) shows the signals of an ethyl group (triplet, 3H at 0.75 ppm, and quartet 2H at 1.47 ppm), of a methyl group on a quaternary carbon atom (singlet, 3H at 0.96 ppm), of four acetoxy groups (singlets at 1.91-2.00 ppm, 12H) and of seven protons of glucose (in the 3.6-5.2 ppm region).

Two singlets are located in the same region. The chemical shifts of the latter (4.0 ppm, 1H, and 3.9 ppm, 2H) permit them to be assigned to $-CH-O-$ and $-CH_2-O-$ groups of the aglycone, respectively, and their multiplicity (singlets) shows that the neighboring carbon atoms lack protons.

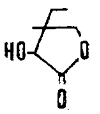
The IR spectrum of (I) (Fig. 2) shows a strong band at 1800 cm^{-1}: it may be due to the presence in the molecule of a γ-lactone or a vinyl ether grouping [1, 2]. For a vinly ether with $C_7H_{11}O_3$ as the composition of the aglycone radical only one variant of the structure of the molecule is possible:



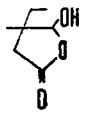
$$\begin{matrix} CH_3-CH_2 \diagdown \\ \qquad\qquad C=CH-OCO-CH_2-O-C_{16}H_{11}O_5, \\ CH_3 \diagup \end{matrix}$$

which we excluded since there is no signal of an olefinic proton in the PMR spectrum of the acetate.

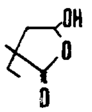
In the case of a β-lactone, six probable structures may be put forward for the aglycone:



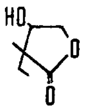
a



b



c



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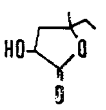
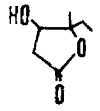


e



f

The absence of spin-spin coupling of the protons in the $-CH_2-O-$ and $-CH-O-$ groupings (see Fig. 1) enables us to exclude structures c, d, e, and f; the chemical shift of the signal of the $-CH_2-O-$ group (3.9 ppm) makes structure *a* most probable for the aglycone, which we have called algin, and, consequently, structure (I) for alginoside.

Analysis of the ^{13}C NMR spectrum (Fig. 3) confirms this assumption. In agreement with the proposed structure, the spectrum of alginoside has the signals of 13 carbon atoms, and in their assignment we used information on their multiplicity obtained from the "off-resonance" spectrum of the protons.

The results of a comparison of the chemical shifts of the carbon atoms 1'-6' with the chemical shifts in various sugars [3] showed that the compounds studied contains a glucosidic fragment in which the substituent occupies the equatorial position, while the chemical shifts of the atoms 1'-6' of the compound investigated and of methyl β-D-glucopyranoside [3] differ by less than 1 ppm (Table 1).

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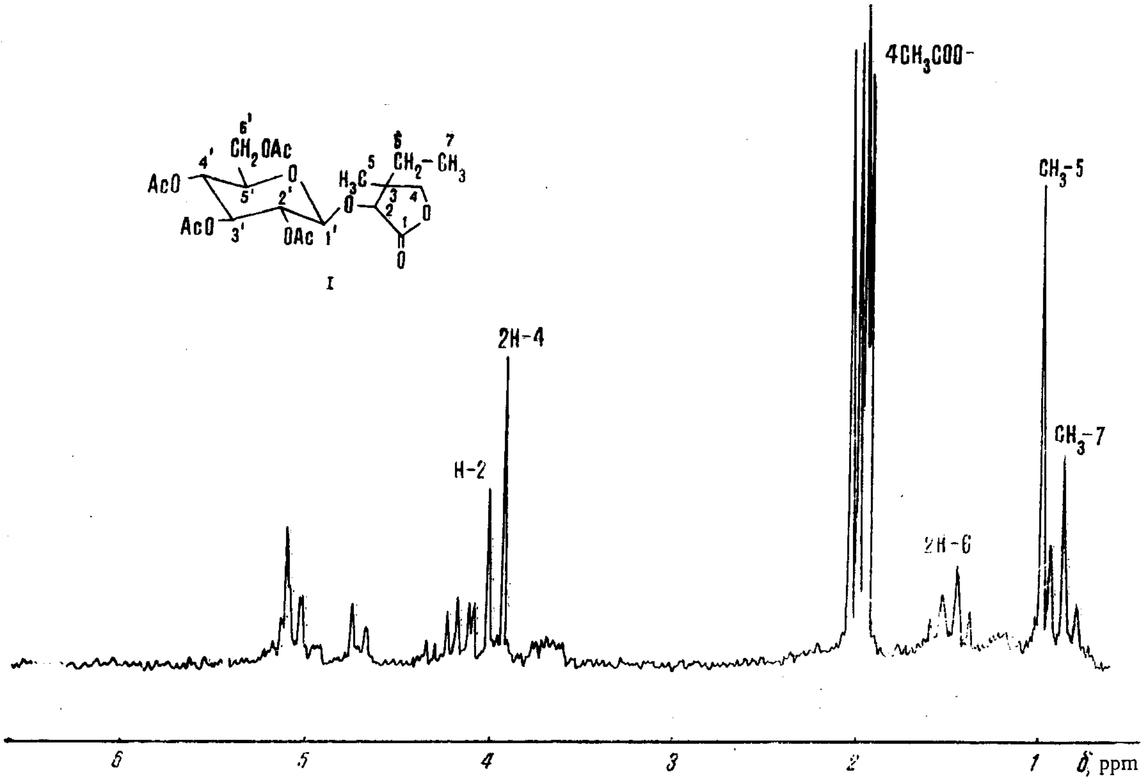

Fig. 1. PMR spectrum of the tetraacetate of alginoside ($CDCl_3$).

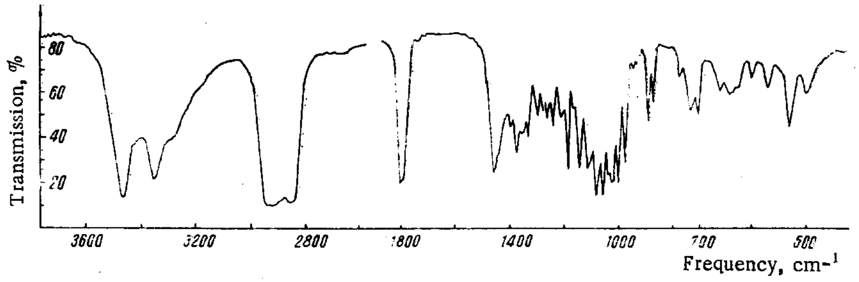

Fig. 2. IR spectrum of alginoside (paraffin oil).

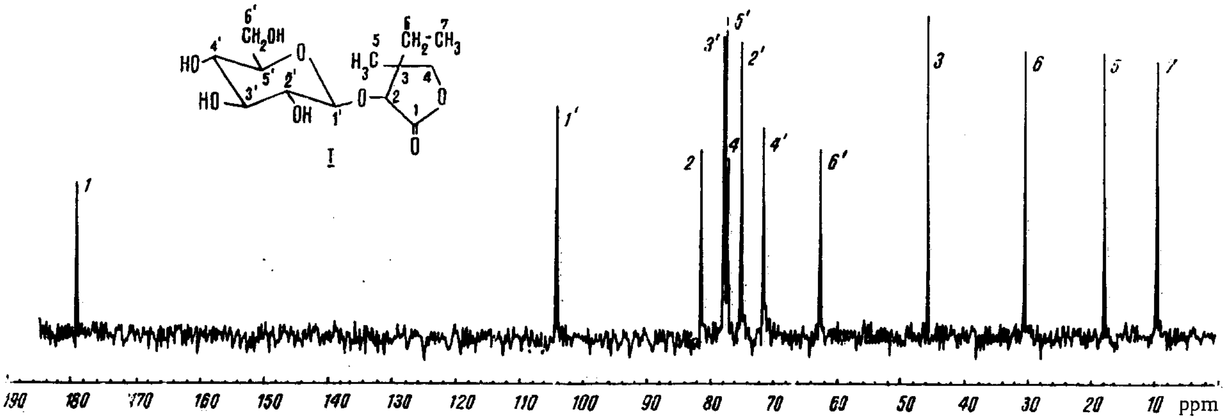

Fig. 3. ^{13}C NMR spectrum of alginoside.

In order to assign the signals of the other seven carbon atoms we took various model compounds (see Table 1). The presence in the spectrum of the signal of a carbonyl carbon (176.46 ppm) of the signals of

TABLE 1. Chemical Shifts of the ^{13}C Nuclei of Alginoside in Comparison with Model Compounds

Alginoside			Model compounds	
No. of the carbon atoms	chemical shifts*	multiplicity from off-resonance	chemical shifts	literature data
1′	103,99	Doublet	104,1	Methyl β-D-glucopyranoside [3]
2′	74,87		74,0	
3′	77,65		76,8	
4′	71,28		70,6	
5′	77,41		76,8	
6′	62,49	Triplet	61,8	
1	179,46	Singlet	182,3;182,7	Spectra 424,423[4]
2	81,25	Doublet	—	—
3	45,56	Singlet	44,3	Spectrum 427 [4]
4	77,01	Triplet	78,6	Spectra 424, 425 73 [4]
5	17,74	Quadruplet	17,9	Spectrum 125 [4]
6	30,31	Triplet	29,3; 36,5	Spectra 207, 206 [4]
7	9,34	Quadruplet	8,8	Spectrum 206 [4]

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*Here and below the chemical shifts are given in ppm from tetramethylsilane, the signal of which was taken as 0.

methyl (17 and 74 ppm) and ethyl (CH_3 – 9.34; CH_2 – 30.31 ppm) groups, and the position of the signals from C_4 (77.0 ppm), C_2 (81.25 ppm), and C_3 (45.56 ppm) show that compound (I) includes a γ-lactone ring. The opposite positions of the substituents at C_2 and C_4 (for example, if the aglycone had structure b) would shift the C_4 doublet into a weaker field (~100 ppm) and the C_2 triplet to approximately 50 ppm [5].

Thus, the association of facts given indicates that alginoside has the structure of α-(β′-glucopyranosyloxy)-β-ethyl-β-methylbutyrolactone (I), and consequently algin is β-ethyl-α-hydroxy-β-methylbutyrolactone.

EXPERIMENTAL METHOD

The IR spectra were taken on UR-20 spectrometer in paraffin oil and in CCl_4 solution, the UV spectra on a Hitachi EPS-3T instrument in methanol, and the PMR spectrum on a Varian HA 100D instrument (with HMDS as internal standard) the α_D values were determined on a AI-EPL polarimeter and the melting points on a Kofler block. The mass spectra were obtained on a Varian CH-8 instrument with the direct introduction of the sample at 75 eV. The recording temperature was 150° C for alginoside and 18° C for algin.

The ^{13}C NMR spectra were taken on a Varian XL-100-15 instrument with the working frequency of 25.16 MHz for ^{13}C nuclei under the conditions of complete and incomplete decoupling from protons at 70° C. The sample was prepared in a 12-mm tube in the form of a 16% solution of compound (I) in water; a 5-mm insert containing D_2O was used to stabilize the resonance conditions.

The purity of the substances was checked by TLC on Woelm silica gel in the chloroform–methanol (3 : 1) system, the spots being revealed with 25% H_2SO_4 at 120° C.

The elementary analyses agreed with the calcuated figures.

Isolation of Alginoside (I). The epigeal part of Rhodiola algida (194 g) was extracted by heating with ethanol (3 × 1 liter). The residue after the distillation of the ethanol was chromatographed on a column containing polyamide powder in a chloroform–methanol gradient system. The 5% methanol eluates were evaporated and the residue was recrystallized from ethanol giving 0.39 g (0.2%) of alginoside, with the composition $C_{13}H_{22}O_8$, mp 192° C. $[\alpha]_D^{20}$ –31.0° (1.8; water), mol. wt. 306 (mass spectrometry), λ_{max} 219 nm (ε 78), R_f 0.7.

Preparation of the Acetate (I). A mixture of 15 mg of (I), 0.3 ml of pyridine, and 0.5 ml of acetic anhydride was kept at 20° C for 24 h. On the addition of ice water, a precipitate of the tetraacetate deposited with the composition $C_{21}H_{30}O_{12}$, mp 147° C (from ether), ν_{CO} 1800 and 1750 cm^{-1}.

Enzymatic Hydrolysis. A solution of 5 mg of (I) in 0.5 ml of water was mixed with a solution of 5 mg of β-glucosidase in 0.5 ml of water, and the mixture was kept at 37° C for 24 h. Glucose was found in the hydrolyzate by paper chromatography in several systems and by TLC on silica gel. The aglycone was extracted with ether, the extract was dried over Na_2SO_4 and evaporated, and liquid was obtained with bp 118° C, R_f 0.6, ν_{CO} 1800 cm^{-1}.

Acid Hydrolysis; Preparation of Algin. A solution of 15 mg of (I) in 2 ml of 2% HCl was heated at 100° C for 40 min. The course of the hydrolysis was monitored by TLC. The aglycone was extracted with ether. Evaporation of the dried extract yielded a faintly yellowish liquid with the composition $C_7H_{12}O_3$, bp 116° C, n_D^{20} 1.4670, mol. wt. 114 (mass spectrometry), R_f 0.6, ν_{CO} 1800 cm^{-1}.

SUMMARY

From *Rhodiola algida* we have isolated a new γ-lactone – alginoside (I) with the composition $C_{13}H_{22}O_8$, mp 192° C. It has been shown that it has the structure of β-ethyl-α-(β'-D-glucopyranosyloxy)-β-methylbutyrolactone.

The aglycone algin obtained by the hydrolysis of (I) is also a new compound, and it has the structure β-ethyl-α-hydroxy-β-methylbutyrolactone.

LITERATURE CITED

1. D. Felix, A. Melera, J. Seibl, and E. Sz. Kovats, Helv. Chim. Acta, 46, 1513 (1963).
2. L. Bellamy, Infrared Spectra of Complex Molecules, 2nd ed., Methuen, London (1958).
3. D. E. Dorman and J. D. Roberts, J. Amer. Chem. Soc., 92, No. 5, 1355 (1970).
4. F. L. Johnson and W. C. Jankowski, Carbon-13 NMR Spectra, Wiley, New York (1972).
5. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley-Interscience, New York (1972).