ADONIS GLYCOSIDES

III. ADONYLIC ACID

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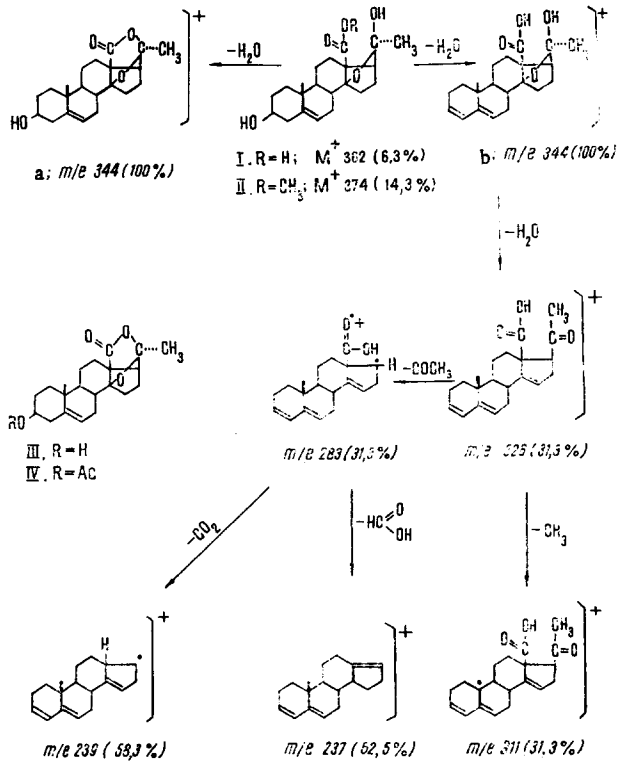
In recent years, the number of examples in which pregnanes have been found in plants together with cardiac glycosides has increased. In the present paper we give the results of a study of a pregnane compound obtained by fractionating the products of the hydrolysis with 0.1 N sulfuric acid of a chloroform extract (fraction B in [1]) from the roots of Adonis chrysocyathus Hook, f. et. Thom.



The composition of the aglycone (I) was $C_{21}H_{30}O_5$, mp 203-205°C (from aqueous methanol), $[\alpha]_D^{25}$ +57.2 ±5° (c 0.29; chloroform). With $SbCl_3$ (I) gives a pink coloration, and with conc. H_2SO_4 a red-brown coloration changing to green. The optical rotatory dispersion curve of the substance is smooth with no Cotton effect, ν_{max}^{KBr} 3400 cm^{-1} 1725, 1450, 1280, 1110, 1050, 930 cm^{-1}. Compound (I) dissolves in sodium carbonate solution and is methylated by diazomethane, which suggests the presence of a carboxy group in it. The composition of the methyl ester of (II) is $C_{22}H_{32}O_5$, mp 200-202°C (from methanol), ν_{max}^{KBr} 3455, 1705, 1450, 1375, 1220, 1135, 1017, 945 cm^{-1}. In the NMR spectrum of (I) (in C_5D_5N, 100 MHz, internal standard HMDS,

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δ scale) there are two three-proton singlets at 0.95 and 1.62 ppm; the first of these signals is apparently due to the protons at C_{19}. The second has a considerable downfield shift apparently because of the combination of a CH_3 group with an oxygen function. In addition, the NMR spectrum has the signal of a vinyl proton at 5.28 ppm and a complex multiplet at 3.67 ppm which obviously corresponds to the proton geminal to the 3β-OH group.

The NMR spectrum of compound (I) is very close to that of adonylide (III) a pregnane compound from Adonis amurensis Regel et Radd. [2]. The compounds compared differ only by the fact that substance (I) is an acid and adonylide is the lactone of this acid. Consequently, we have called the compound that we isolated adonylic acid.

When the acid (I) was acetylated with acetic anhydride in pyridine, a mixture of three acetates was formed, one of which, with lactone absorption (ν_{max}^{KBr} 1775 cm^{-1}) must correspond to the 3-O-acetete of adonylide (IV).

The mass spectrum of adonylic acid (I) corresponds to the proposed structure. The initial stage of the fragmentation of (I) under the action of electron impact is the formation of ions *a* and b with m/e 344. Ion *a* undergoes decomposition according to the scheme given by Shumizu et al. [2], forming peaks with m/e 326 (31.3%), 300 (37.5%), 257 (66.6%), 239 (58.3%). The decomposition of ion c is shown in the scheme given above.

LITERATURE CITED

1. N. K. Abubakirov and R. Sh. Yamatova, Zh. Obshch. Khim., 31, 2424 (1961).
2. J. Shumizu, J. Sato, and H. Mitsuhashi, Chem. Pharm. Bull. (Japan), 15, 2005 (1967).