aluminum hydride in benzene, the carbonyl group and the double bond were reduced. In the IR spectrum of the product obtained, with mp 207–208° C ($C_{30}H_{52}O_5$), the absorption bands at 1650 and 1725 cm^{-1} had disappeared. It is known that such hydrogenation of a double bond is possible only in the case of the conjugation C=C–C=O [1,2].

The IR spectrum also confirms the presence of such conjugation in the aglycone, since there are two absorption maxima at 220 mμ (log ε 4.8, 4.1). When treated with acetic anhydride in pyridine, the aglycone formed an acetate $C_{36}H_{54}O_8$ with mp 108–109° C, $[\alpha]_D$ +30° (c 1.5; ethanol), mol. wt. 540–580 (cryoscopy), % $OCOCH_3$ 21 (titration). The percentage of acetyl groups corresponds to three hydroxyls in the genin. However, the absorption band at 3400 cm^{-1} had not disappeared from the IR spectrum of the acetate, which may show the presence of a nonacetylatable OH group.

The genin gave negative Legal and Liebermann-Burchard reactions. The shifts in the absorption maximum in the UV spectrum of the aglycone under the action of 94% sulfuric acid according to Walens were completely different in this case from the shifts characteristic for steroid sapogenins [3].

The IR spectrum of the aglycone is extremely similar to the spectra of triterpene compounds as is also indicated by the empirical formula given above.

REFERENCES

1. J. F. Me Ghie and J. F. Cavalla, Chemistry and Industry, 744, 1950; J. Chem. Soc., 834, 1951.
2. R. B. Woodword, F. Sondheimer, D. Taub, K. Heusler, and W. M. Me Lamire, J. Am. Chem. Soc., 74, 7223, 1952.
3. H. A. Walens, A. Turner, and M. E. Wall, Anal. Chem., 26, No. 2, 325, 1954.

2 December 1968

Arbuzov Institute of Organic and Physical Chemistry AS USSR

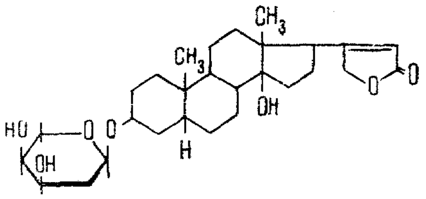
UDC 547.92+615.711.5

DIGITOXIGENIN 3-α-L-ARABINOSIDE

S. G. Kislichenko, I. F. Makarevich, and D. G. Kolesnikov

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 5, pp. 453–454, 1969

Bliss and Ramstand [1], using preparative paper chromatography, have isolated from Evonymus atropurpurea Jacq. in the amorphous state a cardiac glycoside evatroside and have characterized it as digitoxigenin L-arabinosido-D-glucoside. The enzymatic hydrolysis of this compound yielded the monoglycoside digitoxigenin L-arabinoside (evatromonoside). However, evatromonoside was not obtained in the crystalline state. The work of the authors mentioned induced us to synthesize digitoxigenin L-arabinoside in order to decide the presence or absence of this glycoside in the central Russian geographic race of European euonymus (Evonymus medirossica Klok.), the cardenolide composition of which we are engaged in studying [2, 3].



Digitoxigenin 3-α-L-arabinopyranoside was synthesized by the Königs-Knorr method [4] by the reaction of the aglycone digitoxigenin with O-acetyl-L-arabinosyl bromide. The glycoside triacetate formed was saponified with ammonia in methanol. After being freed from accompanying substances by chromatography on alumina and crystallization from water, the glycoside was obtained in the pure state. It melted at 165–168° C; $[\alpha]_D^{23}$ +13.8 ± 5° (c 0.4; methanol). It dissolved in concentrated sulfuric acid giving colorations, min: 0) brown; 1) yellow; 15) yellow-orange; 45) red. On acid hydrolysis by Mannich's method [5], it formed digitoxigenin and L-arabinose. The configuration of the glycosidic bond was established by a comparison of molecular rotations using Klyne's rule [6], and the size of the oxide ring for the carbohydrate component on the basis of the stability of the glycoside to hydrolysis with dilute acids [7, 8].

A careful chromatographic investigation of the combined cardenolides from Evonymus medirossica Kloc., using the digitoxigenin L-arabinoside synthesized as a reference sample, showed that the glycoside is not present in the species of euonymus that we are investigating.

REFERENCES

1. C. A. Bliss and E. Ramstand, J. Amer. Pharmaceut. Assoc., 46, 15, 1957.
2. S. G. Kislichenko, I. F. Makarevich, and D. G. Kolesnikov, KhPS [Chemistry of Natural Compounds], 2, 440, 1966; 3, 241, 1967; 5, 193, 1969.
3. S. G. Kislichenko, I. F. Makarevich, I. P. Kovalev, and D. G. Kolesnikov, KhPS [Chemistry of Natural Compounds], 5, 386, 1969 [in this issue].
4. W. Königs and E. Knorr, Ber., 34, 957, 1901.
5. C. Mannich and G. Siewert, Ber., 75, 736, 1942.
6. W. Klyne, Biochem. J., 47, No. 4, xli, 1950.
7. T. Reichstein, Angew, Chem., 63, 412, 1951.
8. A. Hunger and T. Reichstein, Helv. Chim. Acta, 35, 1973, 1952.

21 April 1969

Khar'kov Chemical and Pharmaceutical Scientific-
Research Institute

UDC 547.944.1

THE STRUCTURE OF SPIREINE

V. D. Gorbunov, A. I. Ban'kovskii, M. E. Perel'son, and O. S. Chizhov

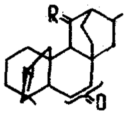
Khimiya Prirodnykh Soedinenii, Vol. 5, No. 5, p. 454, 1969

The isolation from Spireae japonica of a new alkaloid spireine $C_{22}H_{27}O_4N$ with mp 230° C (from ethanol) has been reported previously [1].

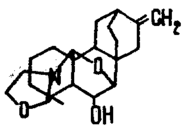
The molecular weight, determined mass-spectrometrically (M^+ ion, m/e 369), is in agreement with the empirical formula of spireine. The molecule of spireine contains two keto groups in unstrained rings (1727 cm^{-1}), a tertiary amide grouping (1683 cm^{-1}), and a tertiary hydroxyl group (3425 cm^{-1}), as is shown by a study of the IR spectra of spireine, its hydrochloride, and its dihydro and tetrahydro derivatives with the measurement of the integral intensities of the carbonyl bands.

The NMR spectra of spireine and its derivatives have shown the presence in its structure of two methyl groups on quaternary carbon atoms (1.44 and 1.49 ppm) and the groupings $CH_2{=}C\Big\langle$ (4.81 and 4.97 ppm) and $-\overset{|}{\underset{|}{C}}-CH_2-\underset{|}{N}-\underset{|}{C}{=}O$ (δ_1 = 2.05 ppm; δ_2 = 2.47 ppm; J = 9.0 Hz. A study of the NMR and mass spectra of deuterated spireine and tetrahydrospireine shows the presence in it of three hydrogen atoms in $-\overset{|}{\underset{|}{C}}-\underset{|}{CH}-\underset{\overset{\|}{O}}{C}-\underset{|}{CH}-\overset{|}{\underset{|}{C}}-$ or $-\underset{\overset{\|}{O}}{C}-\underset{|}{CH}-\overset{|}{\underset{|}{C}}-$ groupings.

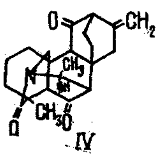
When spireine was heated with selenium at 340° C, a compound (I), $C_{20}H_{27}O_2N$, was obtained. Under similar conditions, Japanese authors [2] obtained compound III from the alkaloid (II) isolated from the same species of Spirea. On the basis of these results and also the IR, NMR, and mass spectra, the structure I may be put forward for the substance $C_{20}H_{27}O_2N$.



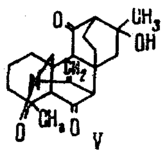
I R = O
III R = 2H



II



IV



V