spatial remoteness of the OH group at C_3 of securigenin from the aldehyde group at C_{10} that is characteristic for aglycones of the cis-A/B series and also by the stability of ring A due to the presence of a double bond in it. Pachygenin, with a spatial arrangement of the A/B rings close to trans, like corotoxigenin [8], readily give the semiacetal form, which is favored by the ready transition of ring A into the boat form.

REFERENCES

1. V. V. Zatula, N. P. Maksyutina, and D. G. Kolesnikov, KhPS [Chemistry of Natural Compounds], **1**, 153, 1965.
2. V. V. Zatula, N. V. Chernobrovaya, and D. G. Kolesnikov, KhPS [Chemistry of Natural Compounds], **2**, 438, 1966.
3. L. Fieser and M. Fieser, Steroids [Russian translation], Moscow, p. 188, 1964.
4. A. Katz, Helv. Chim., Acta, **40**, 831, 1957.
5. L. F. Fieser and T. Goto, J. Am. Chem. Soc., **82**, 1697, 1960.
6. W. Schimid, H. P. Uehlinger, Ch. Tamm, and T. Reichstein, Helv. Chim. Acta, **42**, 72, 1959.
7. V. T. Chernobai, KhPS [Chemistry of Natural Compounds], **1**, 229, 1965.
8. I. P. Kovalev and V. T. Chernobai, KhPS [Chemistry of Natural Compounds], **2**, 179, 1966.

30 July 1968

Khar'kov Chemical and Pharmaceutical Scientific-Research Institute

UDC 547.92+615.711.5

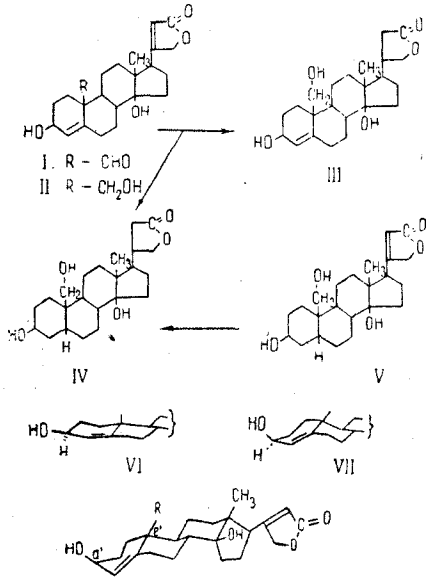
CONFIGURATION OF SECURIGENIN AND SECURIGENOL

V. V. Zatula, I. P. Kovalev, and D. G. Kolesnikov

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 2, pp. 128-129, 1969

The NMR spectrum of securigenin acetate [1] is similar in its main features to the spectra of other cardenolides [2] and differs from the spectrum of strophanthidin acetate [3] only by a signal at 5.59 ppm, which we ascribe to the proton at Δ^4.

The presence of a double bond in ring A imparts a number of special features to the conformation of the molecule of securigenin (I). The difficulty in the formation of a methylal and a semiacetal gives grounds for assuming the presence in the aglycone of a linkage of rings A and B close to the cis form.



The hydrogenation of securigenol (II) over a Pd catalyst [4] did not give satisfactory results. The hydrogenation of securigenol over a more active Pt catalyst [5] in anhydrous methanol gave two products which did not give a positive

Raymond reaction. One of them had properties identical with those of dihydrocannogenol and the other is apparently a dihydrosecurigenol (III). Using preparative paper chromatography, these compounds were separated in the individual amorphous state and some of their properties have been established.

The difficulty of the hydrogenation of the double bond in ring A is probably due to steric hindrance. In view of the fact that Δ^4-steroids can exist in two spatial forms [6], rings A and B in securigenin may be illustrated by two conformational formulas—VI and VII. Depending on the form which the steroid exists in at the moment of hydrogenation, two different products may be obtained—form VI gives the 5α- and VII the 5β-compound. The formation of an intermediate ring between the surface of the catalyst and the compound undergoing reduction is possible only from the less screened side of the molecule. In securigenin this the front side (β-side) from which the approach of the catalyst is freer. In this case, the hydrogen at C_5 takes up the β-configuration, giving dihydrocannogenin [7].

Since the hydrogenation of securigenol in a neutral medium gives dihydrocannogenol (IV) and not dihydrocoroglaucigenin, the most probable conformation for securigenin is VII and not VI.

Thus, securigenin is 3β,14β-dihydroxy-19-oxocard-4,20:22-dienolide and securigenol is 3β,14β,19-trihydroxycard-4,20:22-dienolide. Their structures can be demonstrated by the conformational formulas VIII and IX.

A structure similar to that of securigenin has recently been proposed for hyrcanogenin [8]. Since the aglycone concerned was first isolated from Securigera securidaca [9] and full information on the determination of its structure are reported in the present paper, it appears to us to be right to retain for this compound the trivial name securigenin.

REFERENCES

1. V. V. Zatula, I. P. Kovalev, and D. G. Kolesnikov, KhPS [Chemistry of Natural Compounds], 5, 127, 1969.
2. K. D. Roberts, E. Weiss, and T. Reichstein, Helv. Chim. Acta., 50, 1645, 1967.
3. N. Bhacca and D. Williams, Applications of NMR Spectroscopy in Organic Chemistry [Russian translation], Moscow, p. 65, 1966.
4. B. T. Brown and S. E. Wright, J. Pharm. Pharmocol., 13, 262, 1961.
5. B. Fechtig, G. Euw, O. Schindler, and T. Reichstein, Helv. Chim. Acta, 43, 1570, 1960.
6. A. Nickon and W. L. Mendelson, J. Am. Chem. Soc., 87, 3921, 1965.
7. L. Fieser and M. Fieser, Steroids [Russian translation], Moscow, p. 283, 1965.
8. R. B. Bagirov and N. F. Komissarenko, KhPS [Chemistry of Natural Compounds], 2, 251, 1966.
9. V. V. Zatula, N. P. Maksyutina, and D. G. Kolesnikov, Med. prom. SSSR, no. 11, 21, 1963.

30 July 1968

Khar'kov Chemical and Pharmaceutical Scientific-Research Institute

UDC 547.597+547.918

STRUCTURE OF HELIANTHOSIDE C—A SAPONIN FROM THE SUNFLOWER

P. L. Cheban, V. Ya. Chirva, and G. V. Lazur'evskii

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 2, pp. 129–130, 1969

The chromatography of an acid hydrolysate of helianthoside C [1] on paper and the photocolorometry of chromatograms of the sugars has shown that the monosaccharides of helianthoside C—glucose, arabinose, xylose, and rhamnose—are present in the saponin in a ratio of 2:1:1:3. The molecular weight of the glycoside determined from the yield of the aglycone is 1469.

The saponin and its acetate were treated with diazomethane and the reaction products were subjected to hydrolysis. In both cases, echinocystic acid was isolated, which shows the presence of a O-acyl glycosidic bond in the glycoside. An analysis of the products of the saponification of helianthoside C with alkali showed the presence of a glycoside coinciding in R_f value with helianthoside A.

By chromatography in a thin layer of silica gel and by gas-liquid chromatography the hydrolysate of helianthoside C methylated by Kuhn's method [2] was shown to contain fully methylated glucose, xylose, and rhamnose, 3,4-di-O-methylarabinopyranose, 2,3-di-O-methylrhamnopyranose, and 2,4-di-O-methylglucopyranose. The results of the methylation were confirmed by the periodate oxidation to saponin.

When the permethylated saponin was cleaved with lithium aluminum hydride, derivatives of an oligosaccharide and a glycoside were obtained. The latter was shown to contain completely methylated rhamnose and xylose and also