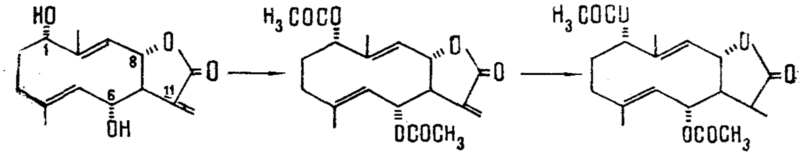
A comparative study of the PMR spectra of tavulin and its derivatives and of tanachin [5] showed that these lactones differ only by the substituent at C_{10}. Apparently, tavulin is isomeric with tatridin A [6-8] and is 1,6α-dihydroxy-1β,6β,7α,8β-H-germacra-4,9,11(13)-trien-8,12-olide:



III V VI

LITERATURE CITED

1. M. Suchy, Collect. Czech. Chem. Commun., 27, 1058 (1962).
2. Z. Samek, M. Holub, et al., Collect. Czech. Chem. Commun., 38, 1971 (1973).
3. A. I. Yunusov, Sh. Z. Kasymov, and G. P. Sidyakin, Khim. Prir. Soedin., 262 (1975).
4. V. A. Mnatsakanyan and L. V. Revazova, Arm. Khim. Zh., 26, 914 (1973).
5. A. I. Yunusov, N. D. Abdullaev, Sh. Z. Kasymov, G. P. Sidyakin, and M. R. Yagudaev, Khim. Prir. Soedin., 462 (1976).
6. F. Shafizadeh and N. R. Bhadane, J. Org. Chem., 37, 274 (1972).
7. F. Shafizadeh and N. R. Bhadane, Phytochemistry, 12, 857 (1973).
8. H. Yoshioka et al., Sesquiterpene Lactones, Chemistry, NMR and Plant Distribution, University of Tokyo Press (1973), p. 158.

STEROID GLYCOSIDES

XXII. ROCKOGENIN GLYCOSIDES

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UDC 547.918+547.917

The preparation from the leaves of Agava americana of glycosides of hecogenin – agavosides – has been reported previously. This plant is one of the sources of steroid glycoside. However, in view of the detection of ever new properties of representatives of this class [2] it is necessary to seek other methods for extending the variety of steroid glycosides.

In the present communication we describe new glycosides obtained by the chemical modification of agavosides A, B, and C'. These compounds were treated with $NaBH_4$ in methanolic solution at 50°C for three hours.

The reaction products were freed from inorganic impurities on Sephadex LH-20 (eluent CH_3OH) and from residues of the starting material on a column of silica gel in the $CHCl_3-CH_3OH-H_2O$ (13 : 5 : 1), system. In all cases the yield was not less than 90%.

The reduction of the keto group in the genin of the agavosides – hecogenin – that took place as the result of the reaction was shown by a study of the products of complete acid hydrolysis of the new compounds. In all cases, the aglycone isolated was identified as rockogenin from its melting point (217-220°C), $[\alpha]_D^{20}$ value (63°), and its R_f value in the presence of an authentic sample [3].

The study of the monosaccharide fraction of the hydrolyzate by paper chromatography and GLC of the aldononitrile acetates derived from the monosaccharides show that the carbohydrate moiety in each of the glycosides had remained unchanged.

Below we give the physicochemical characteristics of the rockosides (aglycone – rockogenin):

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Rockoside	Carbohydrate Composition	mp, °C	$[\alpha]^{20}_D$, deg	R_f*
A	Galactose	233-236	−50	0.76
B	Galactose−glucose (1 :1)	250-253	−40	0.69
C'	Galactose−glucose−xylose (1 :2 :1)	225-228	−75	0.56

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* The R_f values were determined for TLC (L 5/40 silica gel, Chemapol, Czechoslovakia) in the $CHCl_3-CH_3OH-H_2O$ (65 :35 :7) system.

LITERATURE CITED

1. G. V. Lazur'evskii, P. K. Kintya, and V. A. Bobeiko, Dokl. Akad. Nauk SSSR, 224, 1442 (1977).
2. G. V. Lazur'evskii, P. K. Kintya, E. Ch. Pukhal'skaya, and Z. P. Sof'ina, Khim.-Farm. Zh., No. 6, 19 (1977).
3. R. Tschesche and G. Wulf, Fortschr. Chem. Org., Naturst. 30, 481 (1973).

DIOSGENIN AND NEOTIGOGENIN GLUCOSIDES

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UDC 547.918 :547.92

Diosgenin and neotigogenin glucosides have been obtained by the Koenigs−Knorr method [1] in V. T. Chernobai's modification [2].

Acetobromoglucose [3] was condensed with diosgenin and neotigogenin. The reaction products were saponified with a solution of ammonia in methanol. Then chromatography on a column of SiO_2 gave the β-D-glucosides of diosgenin and neotigogenin with yields of 49 and 38%, respectively, reckoned on the genin that had taken part in the reaction.

Neotigogenin glucoside, $C_{33}H_{54}O_8$, had mp 280-281°C (ethanol), $[\alpha]^{30}_D$ −67 ±3° (c 0.79; pyridine). ν^{KBr}_{max}: 3550-3250 (OH), 995, 980, 925 >900, 855 cm^{-1} (spiroketal chain of the 25 S series). NMR spectrum (C_5D_5N), ppm: 0.59 (3 H at C-18, s), 0.76 (3 H at C-19, s), 1.03 (3 H at C-27, d, J = 7 Hz), 1.10 (3 H at C-21, d, J = 6 Hz), 3.30 (H at C-26, doublet with broadened components, J_{gem} = 11 Hz, J_{vic} = 2.5 Hz), 3.80-4.60 (7 H at C-3, C-16, C-26, C-2', C-3', C-4', and C-5', and 2 H at C-6', m), and 4.87 (H at C-1', d, J = 3 Hz − β-configuration of the glycosidic bond [4]). M^+ 578.

Diosgenin glucoside, $C_{33}H_{52}O_8$, had mp 266-268°C (methanol); $[\alpha]^{30}_D$ −96 ±3° c 1.10; pyridine). ν^{KBr}_{max}: 3300-3150 (OH), 980, 960, 920<900, 860 cm^{-1} (spiroketal chain of the 25 R series). NMR spectrum (C_5D_5N), ppm: 0.55 (3 H at C-27, poorly resolved doublet), 0.70 (3 H at C-18, s), 0.78 (3 H at C-19, s), 1.02 (3 H at C-21, d, J = 7 Hz) 3.43 (2 H at C-26, m), 3.70-4.60 (6 H at C-3, C-16, C-2', C-3', C-4', and C-5', and 2 H at C-6', m), 4.85 (H at C-1', d, J = 8 Hz), and 5.20 (H at C-6, m). M^+ 576.

Literature information: mp 269-271°C, $[\alpha]^{20}_D$ −103° (dioxane) [5]. The NMR spectra were taken on a JNM-4H-100 instrument (100 MHz, HMDS, δ scale, ppm), and the mass spectra on a MKh-1303 instrument.

LITERATURE CITED

1. W. Koenigs and E. Knorr, Ber., 34, 957 (1901).
2. V. T. Chernobai, Zh. Obshch. Khim., 34, 1018 (1964).
3. R. L. Whistler et al., Methods in Carbohydrate Chemistry, Academic Press, Vols. I-V (1962-1965).
4. M. Mamsui and M. Okada, Chem. Pharm. Bull., 19, 395 (1971).
5. R. E. Marker and J. Krueger, J. Am. Chem. Soc., 62, 2548 (1940).

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