SUMMARY

Ecdysterone and integristerone A have been isolated from the inflorescences of *Serratula xeranthemoides*.

The amount of these phytoecdysones in the flower heads increases as the plant ripens, reaching a maximum for ecdysterone in the full-flowering phase and for integristerone A at the end of the flowering phase and the beginning of fruit formation.

LITERATURE CITED

1. Yu. D. Kholodova, L. P. Pasternak, and A. I. Apostolov, Ukr. Biokhim. Zh., 48, 533 (1976).
2. The Plant Riches of the Steppe Reserve and the Askaniya-Nova Botanical Park [in Russian], Kiev (1974).
3. Flora of the USSR [in Russian], Moscow–Leningrad, Vol. 28 (1963), p. 270.
4. M. N. Galbraith and D. H. S. Horn, Austral. J. Chem., 22, 1045 (1969).
5. A. A. Akhrem, I. S. Levina, and Yu. A. Titov, Ecdysones — Insect Steroid Hormones [in Russian], Minsk (1973).
6. M. B. Gorovits, I. L. Zatsny, and N. K. Abubakirov, Rast. Res., 10, 261 (1974).
7. U. Baltaev, M. B. Gorovits, N. D. Abdullaev, M. R. Yagudaev, and N. K. Abubakirov, Khim. Prir. Soedin., 813 (1977).
8. Yu. D. Kholodova, Khim. Prir. Soedin., 227 (1977).
9. I. L. Zatsny, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 840 (1971).

TRITERPENE GLYCOSIDES OF *Cauliphyllum robustum*. THE STRUCTURES OF CAULOSIDES b AND c

N. S. Chetyrina and A. I. Kalinovskii

UDC 547.918+547.914

We have detected a series of triterpene glycosides in a methanolic extract from the stems, leaves, and flowers of *Cauliphyllum robustum* Maxim.

From a total methanolic extract of the leaves of this plant by column chromatography on silica gel we have isolated in the individual state two glycosides, which we have called caulosides b (I) and c (II). On acid hydrolysis, each of the caulosides gave hederagenin and a mixture of two monosaccharides. Chromatography on paper showed the presence of L-arabinose and L-rhamnose in both cases.

Caulosides b and c underwent methylation with diazomethane and their IR spectra contained in each case the absorption band of a free carboxy group; consequently, the carbohydrate chain consisting of the monosaccharides mentioned is attached to the hederagenin by a O-glycosidic bond.

Methanolysis of the completely methylated caulosides b (III) and c (IV), obtained by Hakomori's method [1] gave as aglycone the methyl ester of 23-O-methylhederagenin (V) and a mixture of partially methylated methyl glycosides of monosaccharides. The latter were acetylated and analyzed by the chromatographic–mass spectrometric (GLC-MS) method. The results of the analysis of the partially methylated monosaccharides and a determination of the configuration of the glycosidic bonds on the basis of Klyne's rule [2] and the chemical shifts of the carbon atoms of the monosaccharides in the ^{13}C NMR spectrum [3-5] showed for cauloside b the structure of hederagenenin 3-O-α-L-rhamnopyranosyl-1(1 → 2)-α-L-arabinopyranoside, identical with saponin P_D from *Akebia quinata* Decne [6], α-hederin from *Hedera helix* [7], and kalopanax saponin A from *Kalopanax septemlobum* [8].

On partial hydrolysis with 0.4 N sulfuric acid, cauloside c gave two progenins, one of which proved to be identical with cauloside b and the other with cauloside A (VI), which we have isolated previously from the roots of this plant and contains L-arabinose as the sole

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center of the Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 174-176, March-April, 1979. Original article submitted October 10, 1978.

 0009-3130/79/1502-0146$07.50

monosaccharide [19]. The methanolysis of (IV) and analysis of the partially methylated monosaccharides gave methyl 2,3,4-tri-O-methyl-L-arabinopyranoside, methyl 2,4-di-O-methyl-L-rhamnopyranoside, and methyl 3,4-di-O-methyl-L-arabinopyranoside. Analysis of the ^{13}C NMR spectrum of cauloside c permitted assignment of the α configuration to the glycosidic bonds.

According to the facts given above, cauloside c has the structure of hederagenin 3-O-[α-L-arabinopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside].

EXPERIMENTAL

The melting points of the substances were determined on a Boëtius stage, and the optical rotations on a Perkin-Elmer 141 polarimeter. GLC-MC analysis of the methylated monosaccharides was performed on a LKB 9000S instrument. The ^{13}C NMR spectra were taken on a Brüker HX-90 instrument in C_5D_5N.

For column chromatography we used KSK silica gel, 150 mesh, and the toluene–butan-1-ol–water (4:1:to saturation) system. The glycosides were revealed with H_2SO_4. The monosaccharides were chromatographed on type M [" slow"] paper of the "Gosznak" Leningrad mill in the benzene–pyridine–butan-1-ol–water (1:3:5:3) system and were revealed with a solution of aniline phthalate in n-butanol.

Cauloside b (I), mp 258-260°C, $[\alpha]_D^{24}$ +12° (c 0.78; IR, ν_{max}^{KBr}, cm^{-1}: 3350 (OH), 1705 (COOH). $\Delta[M]_D$: (I)-(VI), −160°, rhamnopyranoside: α, −109°; β, +169°. Peracetate, mp 148-150°C (hexane), α_D^{24} +53° (c 1.6; $CHCl_3$). ^{13}C NMR, ppm rel. TMS: C_3 − 81.1, C_{23} − 64.1 (hederagenin); C_1' − 104.3, C_2' − 75.9, C_3' − 74.5, C_4' − 69.3, C_5' − 65.6 (L-arabinose); C_1'' − 101.7, C_2'' − 72.5, C_3'' − 72.5, C_4'' − 74.1, C_5'' − 69.1, C_6'' − 18.6 (L-arabinose).

Cauloside c (II), mp 222-225°C (decomp.), $[\alpha]_D^{24}$ +15.9° (c, 0.94; DMSO). IR, ν_{max}^{KBr}, cm^{-1}: 3350 (OH), 1700 (COOH). Peracetate, mp 158-160°C, $[\alpha]_D$ +39° (c 1.14; $CHCl_3$). ^{13}C NMR (ppm rel DMS): C_3 − 81.2, C_{23} − 64.3 (hederagenin); C_1' − 104.4, C_2' − 75.2, C_3' − 74.9, C_4' − 69.4, C_5' − 66.1 (L-arabinose); C_1'' − 101.2, C_2'' − 72.3, C_3'' − 82.8, C_4'' − 72.9, C_5'' − 69.4, C_6'' − 18.3 (L-rhamnose); C_1''' − 107.2, C_2''' − 72.9, C_3''' − 74.4, C_4''' − 69.4, C_5''' − 67.0 (L-arabinose).

Acid Hydrolysis. Samples of (I) and (II) weighing 50 mg were hydrolyzed with 2 N H_2SO_4 in 50% ethanol. This gave hederagenin, rhamnose, and arabinose.

The hydrolysis of (II) with 0.4 N H_2SO_4 in 50% ethanol (48 h) gave (I), (II), (VI), and hederagenin. The hydrolysis of (I) gave (VI) and hederagenin.

Methylation of (I) and (II). Samples of (I) and (II) weighing 100 mg were methylated by Hakamori's method. This gave 90 mg of the permethylated product (III) with mp 100-115°C, $[\alpha]_D$ + 35° ($CHCl_3$), and 70 mg of the permethylated product (IV), mp 120-122°C (hexane), $[\alpha]_D$ +6.5° (c 0.8; $CHCl_3$). IR spectra: OH absent.

Methanolysis of (III) and (IV). Substances (III) and (IV) (50 mg each) were methanolyzed with 42% HCl_4 in MeOH (1:5, 3 h, 100°C). The reaction mixture was diluted with water, and the precipitate of the aglycone was separated off, washed free from acid, and dried. The methyl ester of 2,3-O-methylhederagenin (V), mp 189-190°C (from ethyl acetate) was identified. After the separation of the aglycone and the neutralization of the acid, the hydrolyzates were evaporated to syrups, dried, and acetylated. GLC-MS showed the presence of methyl 2,3,4-tri-O-methyl-α-L-rhamnopyranoside and methyl 2-O-acetyl-3,4-di-O-methyl-α-L-arabinopyranoside (from III), and of methyl 2,3,4-tri-O-methyl-α-L-arabinopyranoside, methyl 3-O-acetyl-2,4-di-O-methyl-α-L-rhamnopyranoside, and methyl 2-O-acetyl-3,4-di-O-methyl-α-L-arabinopyranoside (from IV).

SUMMARY

Two triterpene glycosides — caulosides b and c — have been isolated from a methanolic extract of the leaves of *Caulophyllum robustum* maxim. Cauloside b has been identified as hederagenin 3-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside, while cauloside c has the structure of hederagenin 3-O-α-L-arabinopyranosyl(1 → 3)-α-L-pyranosyl-(1 → 2)-α-L-arabinopyranoside.

LITERATURE CITED

1. S. Hakomori, J. Biochem., 55, 205 (1964).

2. W. Klyne, Biochem. J., 47, No. 4, xli (1950).
3. T. Usi, J. Chem. Soc., 2425 (1974).
4. P. Colson and R. P. King, Carbohydr. Res., 46, 1 (1974).
5. K. Tori, S. Seo, Y. Yoshimura, M. Nakamura, Y. Tomita, and H. Ishi, Tetrahedron Lett., 4167 (1976).
6. R. Higuchi and T. Kawasaki, Chem. Pharm. Bull., 24, No. 5, 1021 (1976).
7. T. E. Dekanosidze, Khim. Prir. Soedin., 253 (1968).
8. A. Ya. Khorlin, A. G. Ven'yaminova, and N. K. Kochetkov, Dokl. Akad. Nauk SSSR, Ser. Khim., 155, 619 (1964).
9. L. I. Stigina, N. S. Chetyrina, V. V. Isakov, Yu. N. Elkin, A. K. Dzizenko, and G. B. Elyakov, Phytochemistry, 14, 1583 (1975).

TRITERPENE GLYCOSIDES OF *Acanthophllum gypsophiloides*

VI. STRUCTURE OF ACANTHOPHYLLOSIDE D

Zh. M. Putieva, T. T. Gorovich,
E. S. Kondratenko, and N. K. Abubakirov

UDC 547.918:547.914.4

In the present paper we give information on the structure of acanthophylloside D (III), which has been isolated from the roots of *Acanthophyllum gypsophiloides* Rgl. The structures of acanthophyllosides D and C, isolated from this plant previously, have been described in earlier papers [1-3]. Compound (III) was obtained in the individual form after repeated chromatography of the total glycosides.

Unlike acanthophyllosides B and C, acanthopylloside D is not a gypsogenin glycoside. The aglycone precipitating as the result of the hydrolysis of compound (III) is more polar than gypsogenin. The presence of absorption bands in the 2720 and 1720 cm^{-1} regions in the IR spectrum and the peak of an aldehyde proton at 9.47 ppm in the PMR spectrum show that the genin contains an aldehyde group. According to mass spectrometry, the molecular weight of the sapogenin is 486. Furthermore, the substance isolated has a second hydroxy group as compared with gypsogenin. The peak with m/e 264^+ detected in the mass spectrum shows that the hydroxy group is present in ring D or E, and the peaks with m/e 424, 246, and 202 show that it is located at C-16 of the aglycone. An analysis of literature information on the properties of quillaic acid [4-6] and a comparison of them with the results that we have obtained give grounds for considering that the genin of acanthophylloside D is in fact this acid (I). Although there is information in the literature on the presence of quillaic acid in some plants of the family Caryophyllaceae [4, 7, 8], no glycosides of this sapogenin have previously been known.

Investigations of a hydrolyzate by PC, TLC, and GLC showed that the carbohydrate chains of acanthophylloside D include D-glucuronic acid, D-galactose, D-quinovose, D-fucose, L-rhamnose, D-xylose, and L-arabinose in a ratio of 1:2:1:1:1:3:1. After the periodate oxidation of glycoside (III), the D-glucuronic acid, D-fucose, and D-xylose remained unchanged, as in the case of acanthophylloside B [1], which suggested the identity of the structure of the carbohydrate chains of the two compounds compared.

Alkaline cleavage of glycoside (III) gave a tetraoside (II) the carbohydrate chain of which consisted of D-glucuronic acid, D-galactose, and L-arabinose. In the oligosaccharides split off from the carboxy group of the aglycone we detected D-quinovose, L-rhamnose, and D-xylose. The absence of D-fucose from the hydrolysis products showed that it is directly attached to the carboxy group of the genin (I) and was destroyed during the reaction.

The methylation of acanthophylloside D and the hydrolysis of the permethylate obtained led to the same set of methylated monosaccharides as the analogous operation with acanthophylloside B [2, 3].

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 176-180, March-April, 1979. Original article submitted December 12, 1978.

 0009-3130/79/1502-0148$07.50