STEROID SAPONINS AND SAPOGENINS OF Allium

IV. KARATAVIGENIN – A NEW SAPOGENIN FROM Allium karataviense

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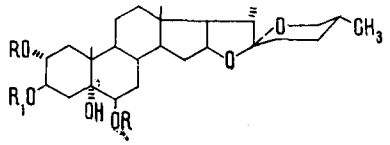
Continuing a study of the steroid compounds of the genus Allium [1-3], we have investigated the bulbs of A. karataviense Rgl. From an ethanolic extract of the bulbs, after treatment with butanol, a glucopyranoside of alliogenin (VI) was isolated. The remaining combined saponins were hydrolyzed, and the genins were separated according to their solubilities in chloroform into two fractions. The chloroform-insoluble fraction yielded alliogenin (I). The other fraction was found by chromatography on alumina to contain diosgenin, yuccagenin, and a new sapogenin (II), which we have called karatavigenin, $C_{34}H_{46}O_7$, mol. wt. 568. On acetylation with acetic anhydride, substance (II) formed a diacetate (III).

The ratio of the densities of the absorption bands in the IR spectrum of the sapogenin (II) at 905 cm^{-1} (strong) and 930 cm^{-1} (weak) permits the genin (II) to be assigned to steroid sapogenins of the 25R series [4, 5]. The absorption in the IR spectrum at 1690 and 1290 cm^{-1}, in combination with the absorption of a benzene ring at 1600, 1585, and 725 cm^{-1}, permits the assumption that in karatavigenin there is an ester grouping of aromatic nature. This is also shown by the intense peaks of ions with m/e 122 ($C_7H_6O_2$) and 105 (C_6H_5O) observed in the mass spectrum of (II).

The nature of the acid residue was found by alkaline saponification of the genin (II). In the acidic fraction of the hydrolyzate benzoic acid was found, and from the neutral fraction a compound identical with alliogenin (I) was isolated.

The methylation of karatavigenin (II) with methyl iodide in dioxane gave a dimethoxy derivative (IV), which, after alkaline hydrolysis, gave the known 3,5-dihydroxy-2,6-dimethoxy genin (V) [2].



I. R=R_1=H
II. R=H; R_1=C_6H_5CO
III. R=Ac; R_1=C_6H_5CO
IV. R=CH_3; R_1=C_6H_5CO
V. R=CH_3; R_1=H
VI. R=H; R_1=$C_6H_{11}O_5$ (D-glucose residue).

Consequently, the benzoic acid residue is attached to the hydroxy group at C_3, and karatavigenin has the structure (II).

EXPERIMENTAL

For general observations, see our previous paper [2].

Extraction of the Plant. The dry bulbs of A. karataviense (5 kg) collected in the phenophase of flowering in May, 1969 (spurs of the Karzhan-Tau range close to the village of Kyzyl-Tan) were extracted with

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ethanol (6 × 10 liters). The extract was evaporated to 2.5 liters, diluted twofold with water, and extracted with butanol (6 × 0.5 liter). Distillation of the butanol yielded 136 g of extractive substances, 102 g of which was dissolved in 750 ml of methanol. The crystals that deposited after brief standing (11.6 g) were identified by their mp of 262-265°C (from methanol–acetone), by their specific rotation of $[\alpha]_D^{20}$ −76.0° (c 1.15; pyridine) and by their IR spectrum as alliogenin β-D-glucopyranoside (VI) [2].

Hydrolysis of the Combined Saponins. To the filtrate obtained after the separation of the alliogenin glucopyranoside were added 200 ml of water and 125 ml of concentrated HCl, and the reaction mixture was heated in the boiling-water bath for 6 h. Then it was diluted with water, and the precipitate that had deposited was filtered off. Weight 30 g.

The combined genins were extracted with chloroform in a Soxhlet apparatus. Evaporation of the solvent from the chloroform extract yielded 13 g of sapogenins (fraction 1). The weight of the insoluble residue was 17 g (fraction 2).

Alliogenin (I). The recrystallization of fraction 2 from a mixture of chloroform and methanol gave 5.5 g of alliogenin with mp 322-324°C, $[\alpha]_D^{20}$ −71.0° (c 1.10; pyridine) [1, 2].

Diosgenin and Yuccagenin. The combined less-polar sapogenins (fraction 1) were separated chromatographically on alumina. When the column was eluted with benzene–methanol (250:1), 215 mg of a sapogenin with mp 198-201°C (from methanol), $[\alpha]_D^{20}$ −131.5° (c 1.14; chloroform) identified as diosgenin [6], was obtained.

Further elution of the column with benzene–methanol (50.1) gave 1.7 g of a sapogenin with mp 238-239°C (from ethanol), $[\alpha]_D^{29}$ −114.7° (c 1.85- chloroform). The acetate of this genin had mp 176-177°C (petroleum ether), $[\alpha]_D^{24}$ − 126.6° (c 1.57; chloroform). This enabled the genin isolated to be identified as yuccagenin [7, 8].

Karatavigenin (II). The subsequent elution of the column with benzene–methanol (50:1 and 30:1) gave 1.4 g of a mixture of sapogenins in which, according to thin-layer chromatography [SiO_2; chloroform–methanol (20:1)], in addition to yuccagenin, there was a more polar genin. The mixture of genins was rechromatographed on alumina, and on elution with benzene–methanol (50:1) 300 mg of (II), $C_{34}H_{48}O_7$, was isolated with mp 277-281°C, $[\alpha]_D^{18}$ −96.8° (c 1.59; pyridine). IR spectrum, cm^{-1}: 3400-3500 (OH), 1690, 1290 (ester grouping), 870, 905 > 930, 990 (spiroketal chain), 1600, 1585, and 725 (benzene ring). Mass spectrum: M^+ 568 (33.5%), 550 (40.4%), 509 (15.5%), 499 (15.5%), 496 (46.2%), 491 (15.5%), 478 (36.3%), 454 (4.7%), 436 (4.7%), 314 (12.2%), 139 (100%), 122 (15.6%), 115 (7.8%), 105 (53.1%).

Karatavigenin 2,6-D-O-acetate (III) from (II). Karatavigenin (II) (100 mg) in 6 ml of pyridine was acetylated with 3 ml of acetic anhydride at room temperature for 48 h. This gave 80 mg of the acetate (III), $C_{38}H_{52}O_9$ with mp 273-276°C, $[\alpha]_D^{18}$ −106.2° (c 1.60; chloroform). IR spectrum, cm^{-1}: 3500-3570 (OH), 1735 (acetyl C=O), 1710 (benzoyl C=O), 870, 910 > 930, 990 (spiroketal chain), 1600, 1585, and 720 (benzene ring). NMR spectrum ($CDCl_3$, HMDS, δ scale): C_{18}, C_{27} 0.74 (6H, s), C_{19} 1.25 (3H, s), C_{26} 3.37 (2H, m), C_{21} 0.89 (3H, δ, J = 6 Hz), C_{16} 4.36 (1H, m), C_6 4.81 (1H, m), C_2, C_3 5.40 (2H, m), and two multiplets at 7.41 and 7.96 ppm of the aromatic protons (5H); mol. wt. 652.

Hydrolysis of Karatavigenin (I) from (II). To 18 mg of karatavigenin (II) in 8 ml of methanol was added 1.5 ml of a 1% methanolic solution of KOH. The reaction mixture was left at room temperature for a day. Then it was acidified with dilute HCl, the precipitate that deposited was filtered off, and the acid hydrolyzate was extracted with chloroform. In the chloroform extract, benzoic acid was detected by thin-layer chromatography [SiO_2; ethanol–ammonia–water (10:1.6:1.2)] [9]. The precipitate obtained was identified by its mp of 318-321°C (from methanol–chloroform), its R_f value on a thin-layer chromatogram [SiO_2; chloroform–methanol (6:1)] and its IR spectrum as alliogenin [2].

Methylation of Karatavigenin (IV) from (II). To 250 mg of (II) suspended in 30 ml of absolute dioxane were added 200 ml of sodium hydride and 2.5 ml of methyl iodide. The reaction mixture was stirred at room temperature for 10 h. Then another 2.5 ml of methyl iodide was added and the mixture was again stirred for 20 h. After this, the solution was acidified with dilute acetic acid and extracted with chloroform. The chloroform extract was washed with sodium bicarbonate solution and with water and was dried and evaporated to dryness. The residue (200 mg) was chromatographed on a column of alumina. Elution with benzene–methanol (500:1) yielded 20 ml of compound (IV), $C_{36}H_{52}O_7$, mp 225-229°C, $[\alpha]_D^{25}$ −110.6° (c 1.03; chloroform). IR spectrum, cm^{-1}: 3500-3520 (OH), 1700 (benzoyl C=O), 870, 910 > 930, 990 (spiroketal chain), 1600 and 725 cm^{-1} (benzene ring); mol. wt. 596.

2α,6β-Dimethoxy-(25R)-5α-spirostan-3β,5α-diol (V) from (IV). To 10 mg of compound (IV) in 8 ml of methanol was added 2 ml of a 2% methanolic solution of KOH, and the mixture was left at 36-37°C for two days. Then it was diluted with water and extracted with chloroform. After the solvent had been distilled off, the dimethoxy derivative (V) was obtained; from its mp of 229-233°C (from acetone), its IR spectrum and its R_f value on a thin-layer chromatogram [SiO_2; benzene–methanol (20:1)] it was found to be identical with an authentic sample of 2,6-dimethoxyalliogenin [2].

SUMMARY

The bulbs of Allium karataviense (family Alliaceae) have been found to contain alliogenin, alliogenin β-D-glucopyranoside, diosgenin, yuccagenin, and a new steroid sapogenin – karatavigenin.

The structure of karatavigenin has been established as alliogenin 3-O-benzoate.

LITERATURE CITED

1. F. S. Khristulas, M. B. Gorovits, V. N. Luchanskaya, and N. K. Abubakirov, Khim. Prirodn. Soedin., 489 (1970).
2. M. B. Gorovits, F. S. Khristulas, and N. K. Abubakirov, Khim. Prirodn. Soedin., 434 (1971).
3. L. I. Éristavi, M. B. Gorovits, and N. K. Abubakirov, Khim. Prirodn. Soedin., 124 (1973).
4. M. E. Wall, C. R. Eddy, M. L. McClennan, and M. E. Klumpp, Anal. Chem., 24, 1337 (1952).
5. C. R. Eddy, M. E. Wall, and M. K. Scott, Anal. Chem., 25, 266 (1953).
6. R. E. Marker, R. B. Wagner, P. R. Ulshafer, E. L. Wittbecker, D. P. J. Cold-Smith, and C. H. Rouf, J. Amer. Chem. Soc., 65, 1199 (1943).
7. R. E. Marker and J. Krueger, J. Amer. Chem. Soc., 69, 2389 (1947).
8. T. Stephen, J. Chem. Soc., 1167 (1956).
9. E. Stahl, Thin-layer Chromatography, Allen, Unwin, and Springer, London (1969).