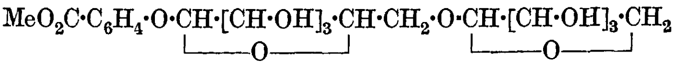
417. *Syntheses of Glucosides. Part IX. Methyl Salicylate Vicianoside (? Violutoside).*

By ALEXANDER ROBERTSON and ROY B. WATERS.

PICCARD (*Compt. rend.*, 1926, **182**, 1167; *Bull. Soc. Chim. biol.*, 1926, **8**, 568; *Schweiz. Apoth.-Ztg.*, 1929, **67**, 341) isolated from *Viola cornuta* a glucoside which he considered to be a vicianoside of methyl salicylate (compare Bridel, *Rev. Gén. Sci.*, 1928, **39**, 5). By the interaction of the 2 : 3 : 4-*O*-triacetyl-β-glucoside of methyl salicylate (Part VIII; J., 1931, 1882) and *O*-triacetylarabinosidyl bromide in the presence of silver oxide in dry benzene we have prepared the *hexa-acetyl*-β-*vicianoside* of methyl salicylate. Deacetylation of this compound gave a product which appears to be identical with violutoside, and is represented thus :



$$MeO_2C\cdot C_6H_4\cdot O\cdot\underbrace{CH\cdot[CH\cdot OH]_3\cdot CH}_{O}\cdot CH_2\cdot O\cdot\underbrace{CH\cdot[CH\cdot OH]_3\cdot CH_2}_{O}$$

O-Hexa-acetyl β-Vicianoside of Methyl Salicylate.—*O*-Triacetylarabinosidyl bromide, m. p. 139°, prepared according to Gehrke and Aichner (*Ber.*, 1927, **60**, 918) is stable for long periods when kept in a vacuum desiccator over soda-lime. Active Ag_2O (6 g.) was added to a solution of the 2 : 3 : 4-triacetyl-β-glucoside of methyl salicylate (3 g., dried at 90°) and *O*-triacetylarabinosidyl bromide (7 g.) in dry C_6H_6 (30 c.c. at 33—34°), and the mixture vigorously agitated for 50 min. and refluxed for 15 min. C_6H_6 (100 c.c.) was then added, and the filtered solution distilled in vac. at 35—40°. To remove the last traces of C_6H_6, the residue was dissolved in Me_2CO (150 c.c.), and the solution evaporated under diminished press. After repetition of this procedure a solution of the almost colourless residual syrup in Me_2CO (50 c.c.) was poured into H_2O (300 c.c.), and the ppt. triturated with cold H_2O until it became solid. A solution of this material in warm MeOH deposited the *hexa-acetate* in colourless rod-like prisms (2·8 g.), m. p. 158° after recrystn., $[\alpha]^{21°}_{5461}$ −42·94° in Me_2CO (*c*, 0·6) (Found : C, 53·4; H, 5·6. $C_{31}H_{38}O_{18}$ requires C, 53·3; H, 5·4%). The compound is readily sol. in $CHCl_3$ or Me_2CO, and is hydrolysed by warm aq.-alc. HCl.

β-Vicianoside of Methyl Salicylate.—The foregoing hexa-acetate (4 g.) quickly dissolved in absolute MeOH (250 c.c.) sat. at room temp. with dry NH_3. After 6 hr., the NH_3 and MeOH were removed under diminished press. and the residue was extracted several times with boiling moist AcOEt. On cooling, the combined extracts gradually deposited the *bioside* in colourless elongated prisms, which were collected 7 days later and recrystallised from the same solvent. The substance was then dissolved in warm 95% Me_2CO and on the addition of Et_2O (2 vols.) gradually separated in needles, m. p. 173° after sintering at 168—169°, $[\alpha]^{21°}_{5461}$ −39·72°, $[\alpha]^{21°}_{5790}$ −36·21° in H_2O (*c*, 0·9) (Found in material dried at 110° in a high vac. for 2 hr. : C, 51·3; H, 5·9. $C_{19}H_{26}O_{12}$ requires C, 51·1; H, 5·8%). Piccard (*loc. cit.*) gives for violutoside m. p. 168·5° (bloc Maquenne), $[\alpha]_D$ −36·2° in H_2O (*c*, 2·84). The glucoside is extremely sol. in H_2O and on slow evaporation of the solution separates as a hydrate in clusters of prismatic needles. It is almost insol. in dry Me_2CO or AcOEt.

This bioside was hydrolysed by emulsin at 37°; after 14 hr., the aq. solution, which had the smell of methyl salicylate, gave a positive $FeCl_3$ reaction, but a control was unchanged.

The authors are indebted to the Chemical Society for a grant.

LONDON SCHOOL OF HYGIENE AND TROPICAL MEDICINE,
UNIVERSITY OF LONDON.
[*Received, October* 11*th*, 1932.]