THE METHYLATION OF GOSSYPETIN 7-β-D-GLUCOPYRANOSIDE

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The classical method of demonstrating the position of a sugar residue in a flavonoid is methylation with subsequent acid hydrolysis of the methyl ether.

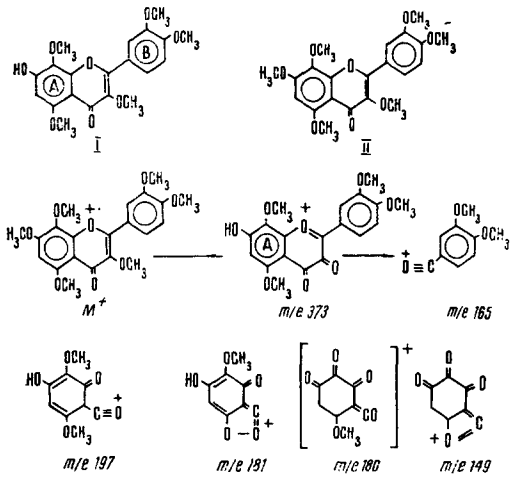
Having isolated from the flowers of the cotton plant of variety 5904-I (G. barbadense) gossypetin 7-β-D-glucopyranoside, in order to determine the position of the glucose in it we have used both methylation and also the proton-magnetic-resonance method [1].

The methylation of gossypetin 7-β-D-glucopyranoside with dimethyl sulfate for 6 h formed an incompletely methylated derivative. When methylation under the same conditions was performed for 30 h, the glucose was split out and the pentamethyl ether of gossypetin (I) with mp 245-246°C was obtained.

The monoacetates of gossypetin pentamethyl ethers described in the literature [2, 3] and those obtained by us did not agree in any properties. To explain the reason for the difference in the melting points of the pentamethyl and hexamethyl ethers and of the monoacetyl derivative of the pentamethyl ether of gossypetin we considered the mass spectra of the pentamethyl ether of gossypetin with mp 245-246°C and of the substance with mp 169°C obtained on its acetylation.

Under the action of electron impact, the gossypetin pentamethyl ether (I) decomposed in the manner of other flavonoids [4, 5]. It gave a molecular peak corresponding to a mass of 388 and the strongest peak of an ion with m/e 373 (M−15) which subsequently decomposed with the formation of an ion with m/e 165.

The position of the free hydroxy group in ring A was confirmed by the presence of an ion with m/e 197. In addition to this, ions with m/e 181, 180, and 149 were formed.



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In the mass spectrum of the substances with mp 169°C, which we [1] and other workers [3] considered to be the monoacetyl derivative of gossypetin pentamethyl ether a molecular peak with m/e 402 is formed, which corresponds to the hexamethyl ether of gossypetin (II). The other peaks in it are also displaced by 14 amu: m/e 387 and 211. In addition, there is a peak of an ion with m/e 149.

For the definitive identification of the substance with mp 169°C as the gossypetin hexamethyl ether obtained by the direct methylation of the aglycone gossypetin, their IR spectra were taken, and these proved to be identical.

Thus, the attempted acetylation of gossypetin 3,3',4',5,8-pentamethyl ether with acetic anhydride under the usual conditions does not give an acetyl derivative but leads to the formation of gossypetin 3,3',4',-5,7,8-hexamethyl ether.

Cases of the migration of intramolecular acetyl groups of flavonoids into the ortho and peri positions have been reported previously [6, 7]. Simpson and Wright [8], using acetoxy-substituted and methoxy-substituted polyphenolic compounds as models, showed the possibility of such rearrangements even in the absence of alkylating agents.

EXPERIMENTAL

Methylation of Gossypetin 7-β-D-Glucopyranoside. A. A mixture of 0.3 g of the flavonol, 50 ml of dry acetone, 3 ml of dimethyl sulfate, and 3.5 g of calcined potassium carbonate was heated under reflux in the water bath for 6 h. Then the potassium carbonate was filtered off and the acetone was distilled off. The residue was diluted with water. On standing, cream-colored crystals with mp 191-192°C (from 8% acetone) deposited which gave a green coloration with ferric chloride. This shows that the substance contains a phenolic hydroxyl.

Found %: C 56.20; H 5.50. $C_{25}H_{28}O_{13}$. Calculated %: C 55.97; H 5.22.

B. A mixture of 0,3 g of the flavonol, 50 ml of dry acetone, 4 ml of dimethyl sulfate, and 4 g of calcined potassium carbonate was heated for more than 30 h (until the reaction with ferric chloride was negative). Crystals were obtained from diluted alcohol in the form of bright yellow needles with mp 245-246°C; the substance did not contain a sugar residue.

Found %: C 61.58; H 5.33. $C_{20}H_{20}O_8$. Calculated %: C 61.85; H 5.15.

Methylation of Gossypetin. Gossypetin (0.4 g) was methylated with dimethyl sulfate as described above for more than 60 h (until the reaction with ferric chloride was negative). Cream-colored crystals with mp 169°C (from 80% ethanol) deposited.

Found %: C 62.95; H 5.66. $C_{21}H_{22}O_8$. Calculated %: C 62.68; H 5.40.

Acetylation of the Methyl Ether of Gossypetin 7-β-D-Glucopyranoside with mp 191-192°C. A mixture of 0.4 g of the methyl ether, 2 g of dry sodium acetate, and 2 g of acetic anhydride was heated in the water bath under reflux for 1 h and was then diluted with cooled water. Crystals were obtained which were filtered off with suction, washed with water until the smell of acetic acid had disappeared, and recrystallized from 80% aqueous acetone; cream-colored needles with mp 169°C deposited.

SUMMARY

On the basis of mass and IR spectra it has been established that the substance with mp 169°C known in the literature as "the acetyl derivative of gossypetin 3,3',4',5,8-pentamethyl ether" is in actual fact gossypetin hexamethyl ether.

Thus, yet another case of the migration of a methoxy group from partially etherified compounds in an alkylation process has been described.

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