Tetrahedron Letters No.16, pp. 1453-1456, 1967. Pergamon Press Ltd. Printed in Great Britain.

TRANSACYLATION IN THE FLAVONOID SERIES. I.
A NEW SYNTHESIS OF COSMOSIIN AND TILIANIN.

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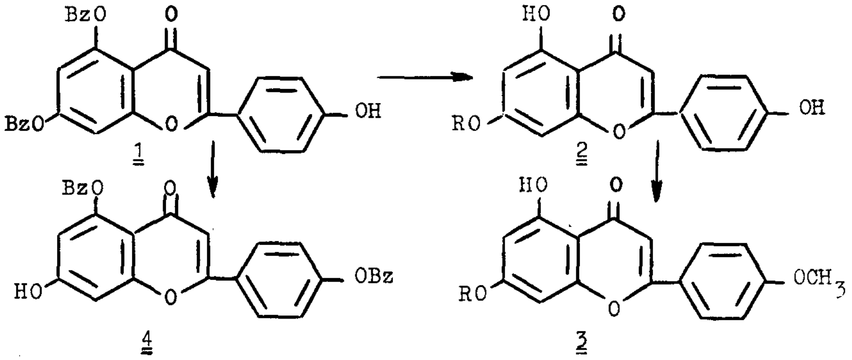
(Received 3 February 1967)

In the course of our investigations in the field of flavonoid-4'-glycosides the synthesis of apigenin-4'-β-D-glucoside 1) was attempted by coupling 5,7-dibenzoyl-apigenin (1) in pyridine with acetobromglucose in the presence of silver carbonate. After the usual work-up and saponification a crystalline glucoside of m.p. 229-321° was obtained in relatively high yield. Spectral characteristics (UV and IR) as well as the m.p. of this compound indicated, that it was not the expected product, but its isomer, apigenin-7-β-D-glucoside (2) or cosmosiin 2), first synthetised by Nakaoki 3).

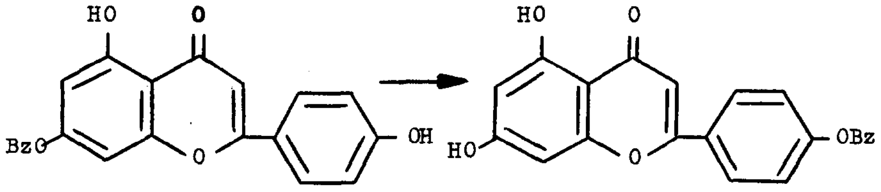


Bz = benzoyl R = -β-D-glucosyl

This was further confirmed by partial methylation leading to acacetin-7-β-D-glucoside (3) 4)(m.p. 259-260°), identified by its m.p., mixed m.p. and by conversion to the pentaacetate of m.p. 206-208° (lit. 4) 208-210°).

This anamalous result promted us to investigate the fate of 1 in the reaction medium. It was found, that in pyridine at room temperature silver carbonate affected a complete isomerisation of 1 into 4',5-dibenzoyl-apigenin (4), (m.p. 272°, acetate m.p. 261-263°). The structure of 4 has been established by methylation (CH_2N_2) to the known 4',5-dibenzoyloxy-7-methoxy-flavone 5) (m.p. and mixed m.p. 216-218°).

An analogous transformation has been experienced with 7-benzoyl-apigenin (5), that was converted under the above mentioned conditions to 4'-benzoyl-apigenin (6) (m.p. 286-288°) as the sole product. Constitution of the latter was abvious from its UV-spectra (bathochromic shift on addition of $AlCl_3$ indicated a free 5-hydroxyl) and by the formation of 5,7-dimethyl-apigenin (m.p. 95°, lit. 6) 298°) on methylation and subsequent saponification.



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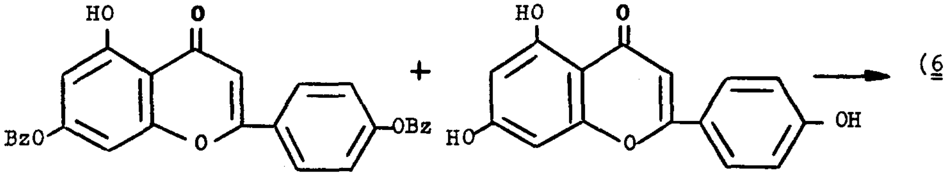
The intermolecular character of these transacylation became apparent from the fact, that a similar treatment of an equimolecular mixture of 4',7-dibenzoyl apigenin (7) and apigenin (8) gave rise in good yield to 6.



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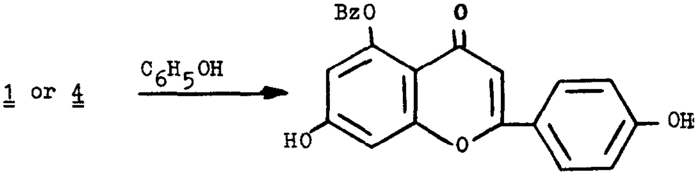
A remarkable resistance of the benzoyl-group attached to the 5-hydroxyl has been observed when 1 or 4 was treated with a large excess of phenol in pyridine-silver carbonate. No cleavage of the 5-benzoyloxy-group has been observed and the main product was 5-benzoyl-apigenin (9) (m.p. 248-249°). Methylation of 9 afforded 5-benzoyloxy-4',7-dimethoxyflavon (m.p. 193-195°), that was saponified to the well known 4',7-dimethyl-apigenin (m.p. 174-176°, lit. 7) 174-176°).



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M.p. determinations of partially benzoylated derivatives on the Koflerblock on glass surface were inconclusive and gave values of 20-30° lower compared to those taken in wide capillary tubes. It was assumed that a transformation, catalysed by the glass surface took place. In fact this reaction could be made a predominant one, when 1 or 4 was mixed thoroughly with glass powder and heated for a short time at 210°. Both afforded in fair yield 4',7-dibenzoyl-apigenin (7) (m.p. 211-212°), identical with a sample prepared by partial benzoylation of apigenin. A similar thermal rearrangement, catalysed by glass surface has been observed with partially acylated sugars by Georg 8).

5,7-dibenzoyl-apigenin (1) (m.p. 247-249°, acetate m.p. 196-198°, methyl-ether m.p. 202-203° (lit. 9) 201°)) was prepared from 4'-benzyl-apigenin 10) via its dibenzoate (m.p. 214-215°). Partial benzoylation of 4'-benzyl-apigenin to 4'-benzyloxy-7-benzoyloxy-flavon (m.p. 198-199°) and subsequent catalytic debenzylation yielded 7-benzoyl-apigenin (5) (m.p. 235-237°).

All new compounds described gave the expected values on elementary analysis.

A detailed communication will follow soon in "Chemische Berichte".

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