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RING ISOMERIZATION OF isoFLAVONE GLYCOSIDES. Part. 1. SYNTHESIS OF TECTORIDIN-4'-METHYL ETHER AND OTHER isoFLAVONE GLUCOSIDES.

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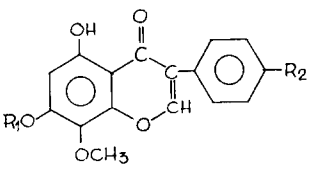
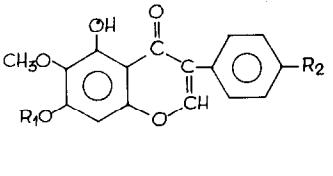
In a preliminary communication [1] we have described a method suitable for the ring isomerization of both polyhydroxy-isoflavones and their O-methyl and O-benzyl derivatives. Later this method has been extended to the group of flavones [2].



I.



II.

a: $R_1=R_2=H$

b: $R_1=H$, $R_2=OCH_3$

c: R_1=tetraacetyl-β-D-glucosyl, $R_2=H$

d: R_1=tetraacetyl-β-D-glucosyl, $R_2=OCH_3$

e: R_1=β-D-glucosyl, $R_2=H$

f: R_1=β-D-glucosyl, $R_2=OCH_3$

We now wish to report that, starting from isoflavone glucosides, substituted in positions 5,7 and 8, we succeeded in synthesising isoflavone glucosides substituted in positions 5,6 and 7 by our method of ring isomerization, this being the first case of ring isomerization of flavonoid glycosides. 5,7-Dihydroxy--8-methoxy-isoflavone /Ia/ [3] and 5,7-dihydroxy-8,4'-dimethoxy--isoflavone /iso-tectorigenin-4'-methyl ether, Ib/ [4] have been coupled with tetraacetyl-α-D-glucosyl bromide in acetonic solution in the presence of concentrated aqueous potassium carbonate to 5-hydroxy-8-methoxy-7-/tetraacetyl-β-D-glucosyloxy/-isoflavone /Ic, mp. 182 C°/ and 5-hydroxy-8,4'-dimethoxy-7-/tetraacetyl-β-D-glucosyloxy/-isoflavone /Id, mp. 194-5 C°/, respectively. Isomerization of the latter by refluxing in alcoholic solution in the presence of potassium carbonate under anhydrous conditions yielded 5-hydroxy-6-methoxy-7-/β-D-glucosyloxy/-isoflavone /IIe, mp. 245-6 C°/ and 5-hydroxy-6,4'-dimethoxy-7-/β-D-glucosyloxy/-isoflavone /IIf, mp. 229-230 C°, lit. [5]: 230°C/, respectively. Acid hydrolysis of the glucosides Ic, Id, IIe and IIf yielded the corresponding aglycones Ia, Ib, IIa /3/ and IIb [4,5], respectively.

Synthetic tectoridin-4'-methyl ether /IIf/ proved to be identical in all respects with the product of methylation of natural tectoridin [5], this being the synthetic proof of the position of the glucosidic linkage of tectoridin which has been proved already previously by degradation [5,6]. Our synthesis proves also the β-configuration of the glucosidic bond.

Experimental details of this work will shortly be published in Acta Chim. Acod. Sci. Hung.

References

1. J. Várady: Tetrahedron Letters. Submitted for publication.
2. J. Várady: Tetrahedron Letters. Submitted for publication.
3. M.L. Dhar and T.R. Seshadri: Tetrahedron 7, 77 /1959/.
4. L. Farkas, J. Várady und Á. Gottsegen: Acta Chim. Hung. 33, 449 /1962/.
5. C. Mannich, P. Schumann und W.H. Lin: Arch. Pharm. 275, 317 /1937/.
6. M. Krishnamurti and T.R. Seshadri: J. Sci. Ind. Research /India/ 13B, 1 /1954/.