ETHYLATION OF QUERCETAGITRIN AND PREPARATION OF ISOPATULETIN PENTAETHYL ETHER

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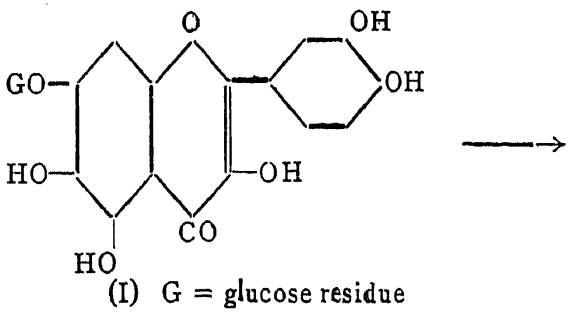
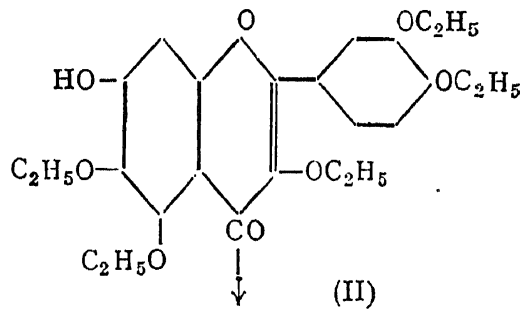
IN a previous paper[1] the constitution of quercetagitrin as the 7-glucoside of quercetagetin, was conclusively proved by providing synthetic evidence. For this purpose the glucoside was completely methylated and hydrolysed and the partial methyl ether thus produced finally ethylated. The reverse of this procedure, *i.e.*, ethylation of the glucoside, hydrolysis of the ethyl ether and final methylation will give a useful derivative not only for comparing it with a similar one obtained from patuletin by ethylation,[2] but also for establishing the constitution of the 7-methyl ether of quercetagetin, called here 'Isopatuletin', if it should occur in nature.

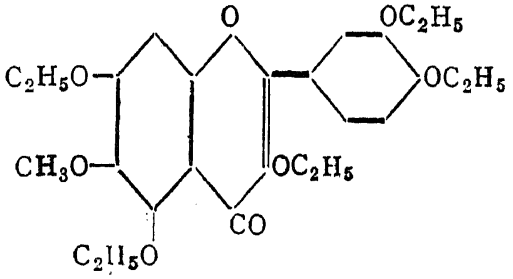
As it has already been mentioned in connection with gossypin[3] the ethylation of glycosides does not proceed satisfactorily with ethyl iodide. Diethyl sulphate is necessary for this purpose. Starting from quercetagitrin (I) the various stages involved in the present study are represented in the following formulæ. The mixed methyl ethyl ether (III) is different from *O*-pentaethyl patuletin (IV). Hence (III) is called iso-patuletin pentaethyl ether. This confirms that quercetagitrin is not a 6-glucoside.



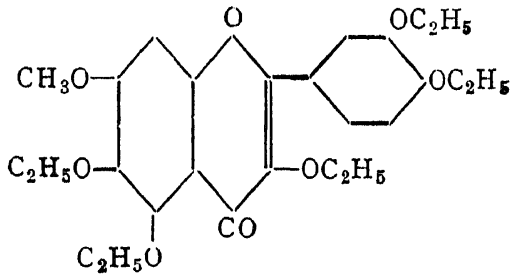
(I) G = glucose residue



(II)



(IV)



(III)

Experimental

Ethylation of quercetagitrin (I)

Quercetagitrin (0·5 g.) was suspended in dry acetone (100 c.c.) and treated with freshly ignited potassium carbonate (6·0 g.) and diethyl sulphate (3 c.c.). After refluxing for 12 hours some more potassium carbonate (2·0 g.) and diethyl sulphate (2 c.c.) were added and the heating continued for a further period of 18 hours. The potassium salts were filtered and washed with warm acetone. From the filtrate the solvent was distilled off and water added. The semi-solid thus obtained was directly hydrolysed as given below.

7-Hydroxy-3 : 5 : 6 : 3′ : 4′-pentaethoxy-flavone (II)

The ethylated glucoside was treated with dilute sulphuric acid (40 c.c.; 7%) and refluxed over a wire-gauze for 2 hours. The solid that separated was filtered and washed with water. The monohydroxy compound crystallised from alcohol as colourless fine needles melting at 175–77°. It dissolved in aqueous sodium hydroxide to give an yellow solution, but did not give any colour with alcoholic ferric chloride. (Found: C, 65·3; H, 6·9; $C_{25}H_{30}O_8$, requires C, 65·5; H, 6·6%). Yield, 0·2 g.

7-Methoxy-3 : 5 : 6 : 3′ : 4′-pentaethoxy flavone (III)

The above 7-hydroxy compound (0·1 g.) was dissolved in dry acetone (15 c.c.) and treated with anhydrous potassium carbonate (2·0 g.) and dimethyl sulphate (0·4 c.c.). After refluxing for 8 hours, the potassium salts were filtered off and washed with warm acetone. On distilling off acetone from the filtrate and adding water to the residue, the monomethoxy-pentaethoxy flavone separated as a colourless crystalline solid. It crystallised from alcohol in the form of fine needles melting at 119–20°. Yield, 0·1 g. 6-Methoxy-3 : 5 : 7 : 3′ : 4′-pentaethoxy flavone[2] (ethyl patuletin) melts at 127–28°. The mixed melting point of the two substances was considerably depressed. (Found: C, 66·2; H, 7·1; $C_{26}H_{32}O_8$, requires C, 66·1; H, 6·8%.)

References

1. Rajagopalan and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1948, **28**, 31.
2. Row and Seshadri .. *Ibid.*, 1946, **23**, 140.
3. Rao and Seshadri .. *Ibid.*, 1947, **26**, 292.