Transformation of Swertiamarin to Gentiopicrin. The Structure of Gentiopicrin

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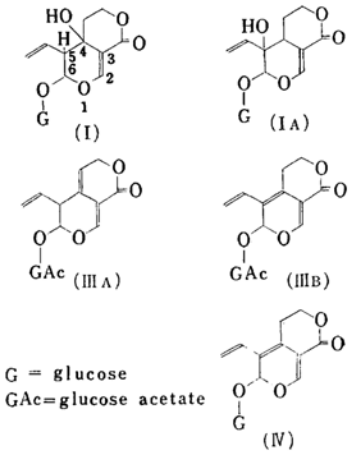
In a preceding communication, it was reported that swertiamarin, the bitter component of *Swertia japonica* Makino, is represented by structure I[1], and that dehydration of the tertiary hydroxyl group of swertiamarin acetate (II) with potassium bisulfate and acetic anhydride affords monoanhydroswertiamarin acetate, $C_{24}\cdot H_{28}O_{13}$ (III), m. p. 143∼144°C which shows bands in its ultraviolet absorption spectrum at 246 mμ log ε 3.44 and 269 μ log ε 3.37[1].

However, on further purification by chromatography and by recrystallization the melting point of II was raised to 151∼152°C (IIIA), and the ultraviolet absorption spectrum showed a band at λ_{max} 245 mμ log ε 3.65 and no band at 269 mμ. On the other hand, II treated with BF_3 in AcOH at low temperature for 3 hr. afforded a dehydrated product (IIIB) as colorless plates, m. p. 137∼138°C. The ultraviolet absorption spectrum showed a band only at 270 mμ log ε 3.8 and none at 246 mμ. Therefore, the monoanhydroswertiamarin acetate (III) described in the previous paper[1] is a mixture of IIIA and IIIB and from the ultraviolet absorption spectra the following formulae are given for IIIA and IIIB respectively. (Fig. 1). The fact that a greater amount of IIIA is produced by the dehydration reaction with potassium bisulfate than the more stable triene type isomer IIIB, indicates the relationship between the hydroxyl group at C_4 and the hydrogen atom at C_5 to be in cis to each other. In the case of the dehydration reaction with BF_3, double bond migration of IIIA occurs by the action of BF_3 and consequently II gives the stable IIIB.



(I) (IA) (IIIA) (IIIB) (IV)

G = glucose
GAc=glucose acetate

Fig. 1

The infrared absorption spectrum of IIIA shows a band at 12.2 μ which is due to the tri-substituted double bond. Therefore the tertiary hydroxyl group of I must exist at C_4 and not at C_5. From these results, an alternative structure of swertiamarin IA[1] can be excluded.

In order to establish the structure of gentiopicrin a detailed study on its degradation reactions was carried out by Asahina, Asano, Tanase and Ueno[2]. On the basis of their data the several possible structures were suggested by Sakurai[3], Korte[3] and Canonica and Pelizzoni[4], respectively. Although, Canonica and Pelizzoni[5] have recently proposed the formula IV as the most probable structure for gentiopicrin, the definite evidence for its carbon skeleton is lacking in their paper. If the structure IV is correct, IIIB, a monoanhydro derivative of II should be identical with gentiopicrin acetate.

Now it has been confirmed that IIIB and the acetate, m. p. 139°C, of gentiopicrin, extracted from the root of ***Gentiana scabrae***, are identical in their infrared absorption spectra.

Concerning the structure of swertiamarin, the correctness of the carbon skeleton of I has been definitely demonstrated by synthesis of erythrocentaurin[6], the hydrolysis product of swertiamarin with emulsin, and by transformation of swertiamarin to gentianin[7] as reported in the previous papers. Although several structures were suggested for gentiopicrin, the structure IV proposed by Canonica and Pelizzoni has been established to be correct from the above-mentioned results.

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