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THE CORRECT STRUCTURE AND SYNTHESIS OF RENGASINE

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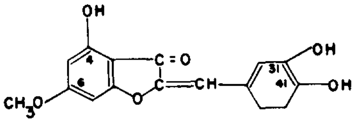
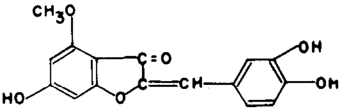
Recently a yellow pigment (rengasine) has been isolated from the heartwood of Melanorrhea spp. (rengas) by F.E. King, T.J. King and D.W. Rustridge who ascribed the structure 2-(3,4-dihydroxybenzilidene)-4-hydroxy-6-methoxy-coumaran-3-one (I) to this compound[1].



I



II

Condensation of 4-hydroxy-6-methoxy-coumaran-3-one[2] with protokatechualdehyde in acetic anhydride, carried out by our method successfully applied to the synthesis of auron glucosides[3], gave 2-(3,4-diacetoxybenzilidene)-4-acetoxy-6-methoxy-coumaran-3-one (m.p. 177-178°, λ_{max} 243 and 383μ), that on saponification according to Zemplen afforded compound I (m.p. 285-287° (decomp.) λ_{max} 258,272 and 329 mμ). Native rengasine* (m.p. 305-306° (decomp.), λ max 254 and 403 mμ, triacetate: m.p.209-210°, λ_{max} 313 and 385 mμ) differed from compound I in every respect.

Therefore it appeared necessary to prepare also the other three monomethylethers of 2-(3,4-dihydroxybenzylidene)-4,6-dihydroxy-coumaran-3-one. The physical constants /m.p. 209-211°, λ_{max} 313 and 382 mμ of 2-(3,4-diacetoxybenzylidene)-6-acetoxy-4-methoxy-coumaran-3-one obtained by the condensation of 6-hydroxy-4-methoxy-coumaran-3-one[4] with protocatechualdehyde proved to be identical with those of the native rengasin triacetate and no depression of m.p. was observed on admixture of the latter. On subjecting the triacetate obtained from the above mentioned condensation to saponification according to Zemplén, compound II formed and crystallized from 80% aqueous methanol with 2 molecules of water. Compound II disclosed with or without crystal water a m.p. of 314-316° (decomp.), (measured in an open capillary), λ_{max} 254 and 403 mμ, and proved to be identical in every respect with the authentic sample.

Consequently, rengasine actually possesses the structure 2-(3,4-dihydroxybenzylidene)-4-methoxy-6-hydroxy-coumaran-3-one (II) instead of the earlier presumed structure I.

A detailed report of these investigations will be published shortly in Chemische Berichte.

REFERENCES

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*Thanks are due to Mr D. W. Rustridge for samples of native rengasine and its triacetate. The m.p. of this sample of rengasine was instead of 220° stated by the mentioned authors, 305°, i.e. nearly identical with that of the synthetic substance.