afforded the free sugar which crystallized in 66% yield from methanol-ether as prisms, m.p. 125–126° (dec.); $[\alpha]_D^{22}$ +10,19° (10 min, equil; *c* 2,03 in water).

Hepta-*O*-acetyl-2-*O*-α-L-rhamnopyranosyl-β-D-galactopyranose (IIb) was prepared in 58% yield from IIa by conversion of the latter to the acetylated glycosyl bromide (IIc), and treatment of the product with mercuric acetate in glacial acetic acid (cf. [11,12]). Pure IIb crystallized from ethanol as colourless needles, m.p. 183–184°; $[\alpha]_D^{25}$ +2,53° (*c* 1,74 in methanol).

Satisfactory analyses were obtained for both anomeric hepta-acetates, and the IR- and NMR-spectra were in conformity with structures IIa and IIb. Neither product possesses physical properties in agreement with those of the compound, m.p. 75–80°; $[\alpha]_D^{19}$ −3,5°, isolated by KUHN et al.[1], and described as a hepta-acetate of 2-*O*-α-L-rhamnopyranosyl-D-galactose. The chromatographic properties reported for the free sugar derived from α-solanine are, however, in close agreement with those of the synthetic product which suggests that the acetate of KUHN et al[1]. might be an impure, amorphous preparation of the β-D anomer (IIb).

Hexa-*O*-acetyl-2-*O*-α-L-rhamnopyranosyl-α-D-galactopyranosyl bromide (IIc), m.p. 98–100°; $[\alpha]_D^{17}$ +121,20° (*c* 3,40 in chloroform) has been employed in the synthesis of naringenin 7-[2-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside] (VI) by a procedure essentially the same as described by AURNHAMMER[13] for the synthesis of flavanone neohesperidosides and rutinosides. Hydrogenation of VI with an equal mass of 10% Pd/C in 8,5% ethanolic KOH under a pressure of 1 bar, yielded the corresponding dihydrochalcone (VII). Compounds VI and VII failed to crystallize, but were obtained pure by chromatography; $[\alpha]_D^{17}$ −66.74° (*c* 4.78 in ethanol) and $[\alpha]_D^{21}$ −83.58° (*c* 2.48 in methanol), respectively.

Organoleptic studies revealed VI to be as bitter as the isomeric neohesperidoside, naringin, and VII to be as sweet as the corresponding naringin dihydrochalcone. The findings of HOROWITZ and GENTILI[14] indicate that the C-3 and C-4 hydroxyl groups of the D-glucose unit are of fundamental importance in determining the taste properties of flavanone and dihydrochalcone neohesperidosides. Similar conclusions were reached by EVANS[15], and BIRCH et al.[16] for other D-glucose derivatives, and the results are in conformity with the hypothesis of SHALLENBERGER and ACREE[17] that the saporous unit of sugars is the α-glycol group, and that its effect is most pronounced when its conformation is synclinal.

Flavanone VI differs from the isomeric naringin merely in respect of the configuration of C-4 of the D-hexose unit which NMR studies indicate to be stabilized in the *C1* conformation in both cases. Moreover, a synclinal conformation of the C-3 and C-4 hydroxyl groups is retained in both compounds, and this might be of particular significance in accounting for the lack of difference in the taste properties of these flavanone glycosides. Similar considerations apply in respect of VII and naringin dihydrochalcone. D-Galactose is, however, itself only about one-half as sweet as D-glucose. This has been ascribed to intramolecular hydrogen bond formation between the axial C-4 hydroxyl group and the ring oxygen atom in D-galactopyranose (*C1* conformation), resulting in less effective intermolecular hydrogen bonding at the taste bud receptor site[17]. If this explanation is correct, the results of the present study indicate that the mechanism is either inoperative in VI and VII, or its effect is greatly outweighed by the taste-enhancing effects of the substituents at C-1 and C-a of the D-galactose units.

Zusammenfassung. Ein acetyliertes, aus α-Solanin gewonnenes Spaltprodukt, das für Hepta-*O*-acetyl-2-*O*-α-L-rhamnopyranosyl-D-galaktopyranose angesehen wurde, stimmt in physikalischen Eigenschaften mit dem α- oder β-Heptaacetat des synthetisch dargestellten Disaccharids nicht überein. Naringenin-7-[2-*O*-α-L-rhamnopyranosyl-β-D-galaktopyranosid] (VI) und das entsprechende Dihydrochalkon (VII) wurden synthetisiert. Flavanon VI ist ebenso bitter wie Naringin, während VII gleichen Süssungsgrad wie Naringin-Dihydrochalkon zeigt.

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Adrenochrome-Thiol Addition Products

Aminochromes, such as adrenochrome (I) react readily with compounds containing an –SH group to give a variety of products (for a list of references see HEACOCK[1] and POWELL et al.[2]). In general three major types of products are formed: a) 5,6-dihydroxyindoles, b) 5,6-dihydroxyindole-4-thioethers and c) aminochrome-thiol addition products. It was suggested, largely on the basis of paper chromatographic and spectroscopic evidence, that the third group of compounds (i.e. the addition products) were structurally similar to the better known adrenochrome-sodium bisulphite addition compound (II)[3,4] in which the bisulphite residue is attached to the 9-position of the aminochrome ring system[5,6].

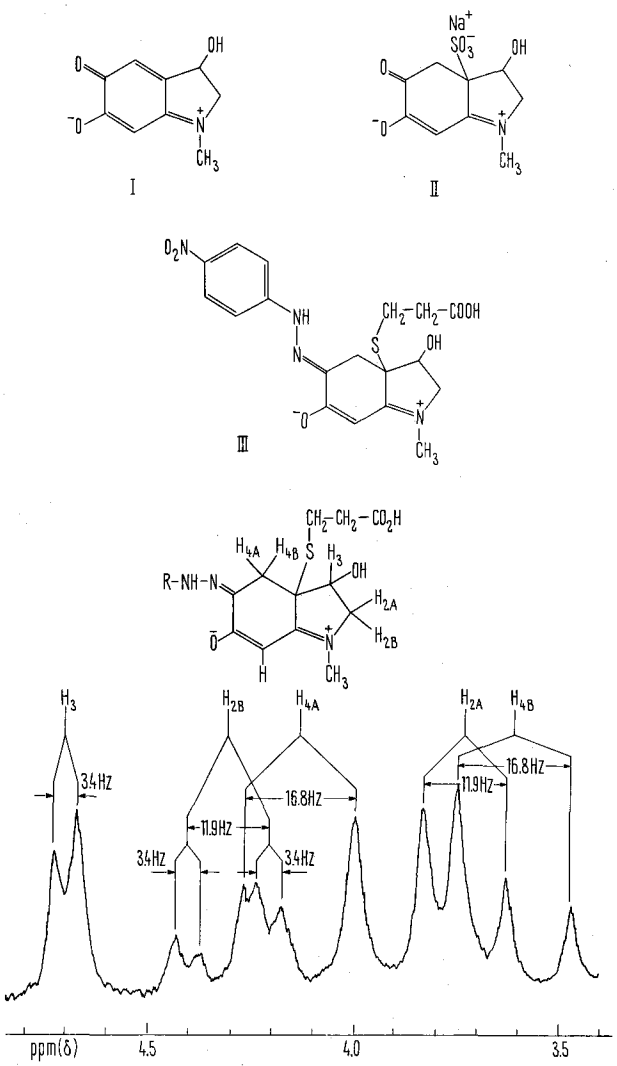
At low pH's the 5,6-dihydroxyindoles and 5,6-dihydroxyindole-4-thioethers predominate; however at mildly acidic or neutral pH's the addition compound appears to be the major product formed. All previous attempts to obtain the latter in solid form have been unsuccessful, due to the ease with which it decomposes on attempted isolation, the thiol-addition products being considerably less stable than the corresponding sodium bisulphite addition products. VAN ESPEN[7] has reported that stable semicarbazones and *p*-nitrophenylhydrazones can be prepared form the adrenochrome-sodium bisulphite addition product. A solid *p*-nitrophenylhydrazone derivative of a typical thiol-aminochrome addition product (i.e. that

obtained by the interaction of adrenochrome (I) and β-mercaptopropionic acid in aqueous sodium acetate) has now been obtained. The structure of the product, i.e. 9-(β-carboxyethylthio)-4, 9-dihydroadrenochrome mono-*p*-nitrophenylhydrazone (III) has been confirmed by microanalytical data and by consideration of its ultraviolet/visible, IR- and NMR- spectra.

Adrenochrome (500 mg) was added to a solution of β-mercaptopropionic acid (593 mg, 2 equiv.) and NaOAc (458 mg, 2 equiv.) in 5 ml H_2O. Nitrogen was bubbled through this solution for about 10 min and it was then added to a stirred suspension of *p*-nitrophenylhydrazine HCl (582 mg, 1.1 equiv.) and NaOAc (254 mg, 1.1 equiv.) in 30 ml H_2O. After stirring the reaction mixture for 20 min, $NaHCO_3$ (1 g) was added cautiously. The resulting mixture was filtered and the filtrate acidified by the dropwise addition of 2*N* HCl to give a light brownish yellow precipitate which was filtered off and dried in vacuo. This material was then triturated with methanol (4–5 ml) and the remaining solid removed by filtration and dissolved in 150 ml of boiling methanol. This solution was filtered and kept overnight at –20° and the resulting small quantity of yellow product which had separated out was filtered off and discarded. Water (150 ml) was added to the filtrate and the resulting solution was concentrated in vacuo to about 150 ml, giving a light brownish yellow microcrystalline solid (320 mg, 27%). The product so obtained could be recrystallized from a methanol/ethyl acetate mixture to give 9-(β-carboxyethylthio)-4,9-dihydroadrenochrome mono-*p*-nitrophenylhydrazone (III) as a yellow microcrystalline solid. On heating, the substance decomposed over a wide temperature range without melting, and it was not possible to obtain a satisfactory melting or decomposition point. λ_{max} (0.1 *M* $NaHCO_3$ aq.) nm (ε): 231 (13,460), 416 (46,400); ν_{max} (Nujol): 3323; 3290 (sh); 1723, 1621, 1607, 1590, 1522, 1503, 1317 cm^{-1}. Anal. Calcd. for $C_{18}H_{20}O_6N_4S$: C, 51.42; H, 4.79; N, 13.33; S, 7.63%. Equiv. Wt. 420. Found: C, 51.48; H, 4.92; N, 13.08; S, 7.54%. Equiv. Wt. 416. The NMR-spectrum showed: δ[Pyridine-d_5/D_2O (5:1)]: 8.40–7.76 (4H, aromatic AA'BB' centered at 8.08); 5.77 (1H, s, H_7); 4.73 (1H, d, X of ABX, $J_{AX} \approx 0$, $J_{BX} = 3.4$ Hz, methine H of –CH (OH) CH_2–); 4.31 (1H, dd, B of ABX, $J_{AB} = -11.9$ Hz, $J_{BX} = 3.4$ Hz); 3.77 (1H, d, A of ABX, $J_{AB} = -11.9$ Hz, $J_{AX} \approx 0$); 4.13 (1H, d, A of AB, J_{AB}, $= -16.8$ Hz, C_4-methylene proton); 3.67 (1H, d, B of AB, $J_{AB} = -16.8$ Hz, C_4-methylene proton); 3.03 (4H, m, A_2B_2, $-CH_2CH_2-$ side chain protons); 2.96 (3H, s, $\overset{+}{\geqslant}N-CH_3$).

The NMR- spectrum of III in pyridine-d_5/D_2O (5:1) in the spectral region δ, 3.4–4.8 is shown in Figure 1.

In this manner it has been possible to confirm the angular attachment of the thiol residue to the aminochrome ring system in a typical aminochrome-thiol addition product. The formation of such addition products may be important in explaining the mechanism of inhibition of certain enzymes by catecholamine oxidation products (cf. References[8–11]).



The NMR-spectrum (60 MHz) of III in pyridine-d_5/D_2O (5:1) using TMS as an internal reference in the region δ (3.4–4.8): R = *p*-Nitrophenyl.

Résumé. Les aminochromes réagissent avec les thiols à des pH neutres ou légèrement acides en donnant des dihydro-4, 9-aminochromes-9-thiosubstitués. On a pu isoler un dérivé *p*-nitrophénylhydrazonique de ce genre de composé et déterminer sa structure à l'aide de la spectroscopie RMN.

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