Phytochemistry, 1964, Vol. 3, pp. 477 to 484. Pergamon Press Ltd. Printed in England

FLAVONOID COMPONENTS OF THE HEARTWOOD OF *PRUNUS DOMESTICA* LINN.

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(*Received* 11 *January* 1964)

Abstract—From the heartwood of *Prunus domestica* the following components have been isolated: (i) a new dihydroflavonol whose constitution is established as 5,7-dihydroxy-4′-methoxy dihydroflavonol (dihydrokaempferide), (ii) a new flavonol prudomestin whose constitution is established as 5,7-dihydroxy-8,4′-dimethoxyflavonol, (iii) kaempferol. Besides these, a second dihydroflavonol and a leucoanthocyanidin have been isolated and are under study. Prudomestin could not be synthesized because its 5-methyl ether is not preferentially demethylated under the usual conditions; its diethyl ether however, has been prepared.

Prunus domestica, which yields the well-known plum fruit, grows in India on the Western temperate Himalayas. Its heartwood is quite durable and is much used in cabinet work, inlay and turnings. In the course of their survey of leucoanthocyanidins Robinson and Robinson[1] examined the heartwood of *P. domestica*, and after heating with alcoholic hydrochloric acid obtained cyanidin and, in much larger quantities, another anthocyanidin, which had the properties of 6-hydroxycyanidin.

In the present work, the flavonoid components of the heartwood of *P. domestica* have been investigated in detail. The wood chips were extracted successively with light petroleum, ether and ethanol. The first extract gave a waxy residue, and the second, which contained flavonoid compounds, was added to the ether-soluble portion of the third. The alcoholic extract was separated into ether-soluble and ethyl acetate-soluble portions. The combined ether extracts were extracted in succession by saturated aqueous sodium bicarbonate, 10% aqueous sodium carbonate, and 0·1% aqueous sodium hydroxide. The bicarbonate-soluble portion consisted of a single compound which was shown to be a new dihydroflavonol, dihydrokaempferide.[2] The carbonate-soluble portion was separated into four components by fractional crystallization. One of these was dihydrokaempferide, and the other three were, a new flavonol, *prudomestin*, kaempferol and a second dihydroflavonol (compound-E). Besides these flavonoid compounds, a leucoanthocyanidin has been obtained from the ethyl acetate-soluble portion of the alcoholic extract. The flavylium chloride obtained from this compound, however, does not correspond with 6-hydroxycyanidin.

Dihydrokaempferide (II)

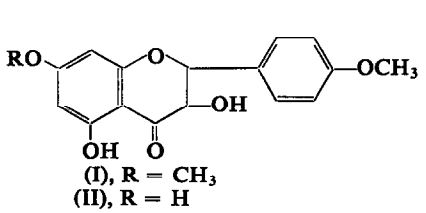
It had the molecular formula $C_{16}H_{14}O_6$ and contained a methoxyl group. Colour reactions, u.v. spectrum (a single maximum at 290 mμ) and i.r. spectrum[3] (carbonyl band at 1639 cm^{-1}) suggested a dihydroflavonol structure, with a hydroxyl group at C_5. The solubility in aqueous sodium bicarbonate was suggestive of a hydroxyl at C_7. The compound formed a

[1] G. M. ROBINSON and R. ROBINSON, *Biochem. J.* **27**, 206 (1933).

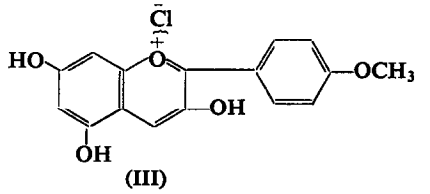
[2] G. R. NAGARAJAN and T. R. SESHADRI, *J. Sci. Ind. Res., India* **20B**, 509 (1961). In this communication the heartwood was referred to as that of *Prunus communis*. *P. domestica* Linn. is now found to be the correct name, synonymous with *P. communis* Huds. (Chopra, *Glossary of Indian Medical Plants*, C.S.I.R. (India) Publication, 1956, p. 205.)

[3] L. H. BRIGGS and L. D. COLEBROOK, *Spectrochim. Acta* **18**, 939 (1962).

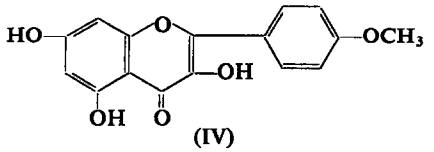
monomethyl ether, which still retained the C_5 hydroxyl group as indicated by the strong ferric chloride colour, the melting point of which agreed with that of 7,4′-*o*-dimethylaromadendrin (I).[4] The original compound was therefore 5,7-dihydroxy-4′-methoxyflavanonol (dihydrokaempferide) (II). The above conclusion was supported by isomerization of the compound (II) into 3,5,7-trihydroxy-4′-methoxyflavylium chloride (III),[5] the identity of which was established by comparison with a sample obtained from kaempferide (IV) by reductive acetylation[5,6] and also with one preparaed by the condensation of *o*-monobenzoylphloroglucinaldehyde and *ω*-acetoxy-*p*-methoxyacetophenone. The structure of (II) was also confirmed by its dehydrogenation to kaemperide (IV) by iodine and potassium acetate.



(I), R = CH_3
(II), R = H



(III)



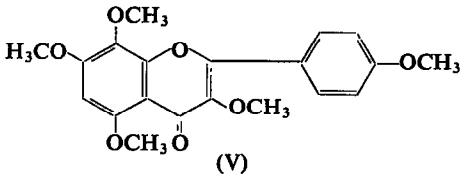
(IV)

Racemic dihydrokaempferide (m.p. 178–180°) was synthesized by reducing kaempferide (IV) with sodium dithionite in alkaline medium.[7] The optically active natural sample (m.p. 204–205°) was racemized and gave a product identical with the synthetic sample.

Prudomestin (VII)

Prudomestin and dihydrokaempferide could be separated from kaempferol and "Compound-E" in the carbonate soluble fraction by the solubility of the former two in hot benzene. Subsequent separation of prudomestin and dihydrokaempferide was effected by the markedly greater solubility of the former in hot chloroform.

Prudomestin had the molecular formula $C_{17}H_{14}O_7$ and contained two methoxyl groups. Its colour reactions and spectral properties suggested a flavonol structure. On prolonged treatment with dimethylsulphate and potassium carbonate in acetone it gave herbacetin pentamethyl ether (V).



(V)

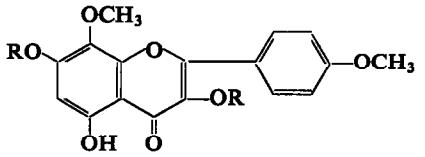
Prudomestin did not respond to the gossypetone test[8] characteristic of a quinol system and was fairly stable in alkaline solution. The presence of a chelated hydroxyl in the 5-position

[4] S. S. SATWALEKER, T. R. GUPTA and P. L. NARASIMHARAO, *J. Indian Inst. Sci.* **39**, 195 (1957).
[5] H. PACHÉCO and M. CHANDENSON, *Compt. rend.* **242**, 1621 (1956); H. G. KRISHNAMURTI, T. R. SESHADRI and B. VENKATARAMANI, *J. Sci. Ind. Res., India* **19B**, 115 (1960); H. G. KRISHNAMURTI, V. KRISHNAMURTI and T. R. SESHADRI, *Phytochemistry* **2**, 47 (1963).
[6] K. R. LAUMAS and T. R. SESHADRI, *Proc. Indian Acad. Sci.* **49A**, 47 (1959).
[7] JOHN C. PEW, *J. Amer. Chem. Soc.* **70**, 3031 (1948).
[8] A. G. PERKIN, *J. Chem. Soc.* 650 (1913).

was evident from the time taken for complete methylation. These observations indicated that one of the methoxyls is at the 8-position.

The u.v. spectrum of an ethanolic solution of prudomestin had maxima at 225, 275, 323 and 375 mμ. On the addition of fused sodium acetate the maximum at 275 mμ suffered a bathochromic shift of 10 mμ indicating the presence of a hydroxyl at the 7-position.[9] The absence of any change on the addition of boric acid and fused sodium acetate showed than an ortho-dihydroxy system was not present,[10] thus supporting the location of a methoxyl at the 8-position. The presence of a free hydroxyl at the 3-position was shown by the large bathochromic shift of 55 mμ of the long wavelength maximum on the addition of aluminium chloride.[11] It was therefore evident that the other methoxyl should be at the 4'-position. This was confirmed by preparing the diethyl ether of prudomestin which on fission with alcoholic potash yielded anisic acid.

Based on these observations the diethyl ether was assigned the structure (VI) and prudomestin* the structure (VII). This is a fourth member of the group of naturally occurring herbacetin methyl ethers, including tambuletin,[12] tambulin[13] and flindulatin.[14]



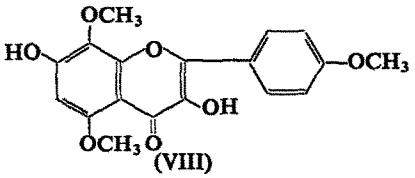
(VI), R = C_2H_5
(VII), R = H

In attempting the synthesis of prudomestin, 3,7-dihydroxy-5,8,4'-trimethoxyflavone (VIII) was prepared as an intermediate by the Allan–Robinson condensation of ω-benzoyloxy-2,4-dihydroxy-3,6-dimethoxy acetophenone with sodium anisate and anisic anhydride. The selective demethylation of (VIII) at the 5-position has not been successful. Aluminium chloride in acetonitrile failed although it may be mentioned that under the same conditions the 5-methoxyl suffers demethylation if the 3-hydroxyl is alkylated. Aluminium chloride in nitrobenzene was also not effective at room temperature, but at 100° demethylation was extensive.[15] Hydrogen bromide in acetic acid at room temperature also failed, though successful selective demethylations of the 5-methoxyl have been reported earlier;[16] but in such cases the 3-hydroxyl again was alkylated. At 100° this reagent brought about extensive demethylation. When this work was in progress, similar failures were reported by Horowitz and

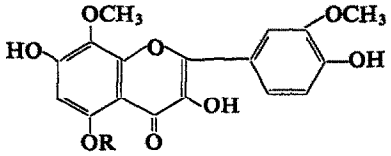
* In a private communication Dr. Masao Hasegawa informed us about the isolation of a new dihydroflavonol glucoside, *prumumenin* from the heartwood of *Prunus mume*, which he believed to have the structure of 7-glucoside of dihydroherbacetin-8,4'-dimethyl ether. The dehydrogenation product of the aglycone is now found to be identical with prudomestin. Therefore the aglycone should be dihydroprudomestin and prumumenin is its 7-glucoside.

[9] L. Jurd and R. M. Horowitz, *J. Org. Chem.* **22**, 1618 (1957).
[10] L. Jurd, *Arch. Biochem. Biophys.* **63**, 376 (1956). In the compounds studied by Jurd, the *ortho* dihydroxy system was present at the side phenyl ring. In order to study the effect of this reagent on a dihydroxy system in the condensed benzene ring, the shift in the case of herbacetin was studied and was found to be 10 mμ (bathochromic shift) of the lower wavelength band.
[11] L. Jurd and T. A. Geissman, *J. Org. Chem.* **21**, 1395 (1956).
[12] K. J. Balakrishna and T. R. Seshadri, *Proc. Indian Acad. Sci.* **25A**, 449; **26A**, 72 (1947).
[13] *Idem; ibid.* **26A**, 296 (1947).
[14] R. F. C. Brown, P. T. Gilham, G. K. Hughes and E. Ritchie, *Austral. J. Chem.* **7**, 181 (1954).
[15] K. Visweswara Rao and T. R. Seshadri, *Proc. Indian Acad. Sci.* **22A**, 383 (1945).
[16] R. C. Shah, V. V. Virkar and K. Venkataraman, *J. Indian Chem. Soc.* **19**, 135 (1942); T. R. Seshadri and V. Venkateswaralu, *Proc. Indian Acad. Sci.* **24A**, 349 (1946).

Gentili[17] in their attempts to synthesize limocitrin (IX) from the flavonol (X) by selective demethylation at the 5-position.



(VIII)



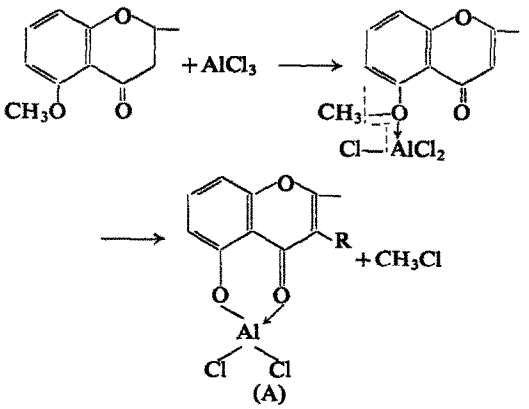
(IX), R = H
(X), R = CH_3

However, for confirmation of the structure of prudomestin, its partial ethyl ether (VI) was synthesized from the trimethyl ether (VIII) by ethylation and subsequent selective demethylation at the 5-position. This demethylation could be successfully effected using aluminium chloride in acetonitrile and the product is identical with the diethyl ether obtained from prudomestin.

Mechanism of Selective Demethylation

From the above studies it can be seen that: (1) Selective demethylation of the 5-methoxyl in a flavonol having the 5,8-dimethoxy system is only successful when the 3-hydroxyl is alkylated; for this purpose aluminium chloride in acetonitrile is quite suitable. (2) If the 3-hydroxyl is free, demethylation of the 5-methoxyl requires more drastic conditions, under which the 8-methoxyl also suffers demethylation.

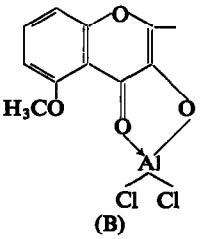
These observations can be explained in the following manner. The normal demethylation of an aryl-alkyl ether by means of aluminium chloride should be facilitated by the presence of an additional group, itself capable of entering into co-ordination with the metal atom, e.g. a carbonyl situated *ortho* to the methoxyl concerned. The facility of demethylation in such a case can be attributed to the formation of a stable cyclic co-ordination complex. A flavonoid with a methoxyl at the 5-position is a typical example of this kind and the demethylation can be represented as shown below.



(A)

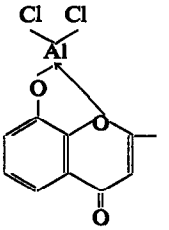
[17] R. M. HOROWITZ and B. GENTILI, *J. Org. Chem.* **26**, 2899 (1961).

When both the 3- and 5-positions of a flavonoid are occupied by methoxyl groups a six-membered ring complex (A) involving the oxygen at the 5-position will be sterically more favoured than a 5-membered ring complex (B) involving the oxygen at the 3-position. Hence a selective demethylation at the 5-position takes place. Recent i.r. data[3] show that the 3-hydroxyl is comparatively only weakly hydrogen bonded with the carbonyl, whereas the 5-hydroxyl is strongly bonded.



(B)

In the case of flavonols having the 3-hydroxyl free and the 5-hydroxyl methylated, the formation of the five-membered ring complex (B) is favoured as it involves only a detachment of the proton, rather than the detachment of a methyl group. This would explain the comparative resistance of the 5-methoxyl to demethylation in such cases. More drastic conditions are therefore required which bring more extensive demethylation involving the 8-methoxyl, presumably due to an analogous complex (C) formation involving the adjacent pyrone ether oxygen.[18]



(C)

EXPERIMENTAL

In circular paper chromatography solvents designated as "A" and "B" were respectively 50% acetic acid and lower layer of butanol–acetic acid–water (4:1:5, v/v).

Extraction of the Heartwood

The heartwood was kindly supplied by the Forest Officer, Baramulla, Kashmir, India. The air-dry heartwood chips (1·2 kg) were extracted in succession with petroleum ether, ether and ethanol at room temperature. The petroleum ether extract yielded only waxy matter. The ether extract consisted of flavonoid components. The alcohol extract was concentrated under reduced pressure to a syrup, exhaustively extracted with ether and then with ethyl acetate. The ether extracts were combined and concentrated and then successively extracted with (i) saturated aqueous sodium bicarbonate, (ii) 10% aqueous sodium carbonate, and (iii) 0·1% aqueous sodium hydroxide. The residual ether extract yielded waxy matter.

The ethyl acetate extract was dried over anhydrous magnesium sulphate, concentrated under reduced pressure and then subjected to fractional precipitation by the addition of dry light petroleum. At first, coloured impurities separated out and finally a buff-coloured mass (9 g) separated which gave tests for leucoanthocyanidin.

[18] Ishwar Dass, N. Narasimhachari and T. R. Seshadri, *Proc. Indian Acad. Sci.* 37A, 599 (1953).

Dihydrokaempferide (II)

Acidification of the bicarbonate extract precipitated a pale yellow solid (0·2 g) which gave only one ring in paper chromatography (R_f values: 0·90 in "A" and 0·63 in "B"). It crystallized from methanol as colourless needles, m.p. 204–205°, $(\alpha)_D^{30}+16°$ (Found: C, 63·3; H, 5·0; OCH_3, 10·3. $C_{16}H_{14}O_6$ requires: C, 63·6; H, 4·6; one OCH_3, 10·3%). Light absorption: λ_{max}^{MeOH} 290 mμ (log ε 4·23); i.r. (Nujol): 1639 cm^{-1}. It gave a purplish brown colour with alcoholic ferric chloride and a deep red colour with both magnesium and hydrochloric acid and zinc and hydrochloric acid.

Kaempferol, Compound E, Dihydrokaempferide and Prudomestin (VII)

The carbonate extract on acidification gave a brownish yellow mass (7·5 g) which was repeatedly extracted with hot benzene. The brown benzene insoluble residue (2 g) consisted of two compounds as revealed by paper chromatography. Resinous impurities were removed by dissolving in ethyl acetate and treatment with light petroleum. After distilling off the solvent under reduced pressure the product was extracted with hot water. The water-insoluble fraction on repeated crystallization from alcohol yielded kaempferol as yellow plates (0·35 g), m.p. 275–276°, alone or admixed with an authentic sample. The identification was confirmed by preparation of the tetraacetate (m.p. 184°).

The water-soluble portion separated as pale brownish yellow solid (Compound E) on cooling, and it crystallized from methanol as prisms (0·2 g), m.p. 239–241°. λ_{max}^{MeOH} 290 mμ; i.r. (Nujol): 1639 cm^{-1}. It developed a pink colour on treatment with zinc and hydrochloric acid. Further study of this compound is in progress.

The benzene-soluble material (4·8 g) from above was fractionated using chloroform. The less soluble portion on crystallization from methanol afforded further quantities of dihydrokaempferide (1 g). The more soluble portion on repeated crystallization from chloroform–light petroleum yielded *prudomestin* as yellow needles (1·5 g), m.p. 209–210° (Found: C, 61·8; H, 4·7; OCH_3, 17·6; $C_{17}H_{14}O_7$ requires: C, 61·8; H, 4·2; two OCH_3, 18·8%). Light absorption: λ_{max}^{EtOH} 225 mμ (log ε 4·34); 275 mμ (log ε 4·35); 323 mμ (log ε 4·13) and 375 mμ (log ε 4·22); i.r. (KBr): 3356 cm^{-1} and 1661 cm^{-1}. It gave a green colour with alcoholic ferric chloride and a deep pink colour with magnesium and hydrochloric acid. It did not respond to the gossypetone test.

Methylation of Dihydrokaempferide

A solution of (II) (0·1 g) in acetone (100 ml) was refluxed with dimethyl sulphate (1 ml) and anhydrous K_2CO_3 (0·5 g) for 14 hr. The product crystallized from ethyl acetate–light petroleum as colourless needles melting at 187–188° agreeing with the melting point reported in the literature[4] for (I). It gave a brown colour with alcoholic ferric chloride.

3,5,7-*Trihydroxy*-4′-*methoxyflavylium Chloride (III)*

(*a*) *By direct synthesis.* A solution of *o*-benzoyl phloroglucinaldehyde (75 mg) and ω-acetoxy-*p*-methoxy acetophenone (60 mg) in ethylacetate (20 ml) was cooled and saturated with dry HCl gas for 5 hr and then kept at 0° for 2 days. The reddish brown solid product was washed with dry ether. The product was debenzoylated by keeping with 10% aqueous alcoholic NaOH (15 ml) in an H_2 atmosphere for 3 hr with occasional shaking. After the addition of concentrated HCl, the mixture was heated at 60° for some time and kept at 0° for a day. The dark red precipitate was collected, washed with dilute HCl followed by ether and dried. The crude flavylium chloride crystallized from a mixture of EtOH and dilute hydrochloric acid as deep red needles; $\lambda_{max}^{EtOH-HCl}$ 523 mμ; R_f values: 0·86 and 0·58 in "A" and "B".

(*b*) *From dihydrokaempferide.*[5] A mixture of dihydrokaempferide (0·05 g), acetic anhydride (5 ml) and fused potassium acetate (0·2 g) was refluxed for 1 hr. The resulting *pseudo* base acetate was converted into the flavylium chloride by boiling with 10% alcoholic hydrochloric acid (30 ml). R_f values: 0·86 and 0·58 in "A" and "B".

(*c*) *From kaempferide.*[5,6] Kaempferide (0·05 g) was subjected to reductive acetylation using zinc dust (0·2 g), fused sodium acetate (0·1 g) and acetic anhydride (5 ml). The product thus obtained gave the flavylium chloride on boiling with 10% alcoholic hydrochloric acid (30 ml). $\lambda_{max}^{EtOH-HCl}$ 525 mμ; R_f values: 0·86 and 0·58 in "A" and "B".

Dehydrogenation of Dihydrokaempferide to Kaempferide

A mixture of dihydrokaempferide (0·2 g) and fused potassium acetate (1·0 g) in glacial acetic acid (10 ml) was heated under reflux and iodine (0·2 g) in glacial acetic acid (10 ml) was added in small lots during 1 hr. After refluxing for a further 3 hr, acetic acid was removed under reduced pressure and SO_2 water added to the residue. The product crystallized from benzene as yellow needles (0·1 g), m.p. 220–221° alone or when mixed with a synthetic sample of kaempferide. With alcoholic ferric chloride it gave a green colour with brownish tinge. With concentrated sulphuric acid it exhibited a greenish blue fluorescence. Light absorption: λ_{max}^{MeOH} 222 mμ (log ε 4·33); 267 mμ (log ε 4·27) and 320 mμ (log ε 4·08); i.r. (Nujol): 3356 cm^{-1} and 1661 cm^{-1}.

Reduction of Kaempferide to Dihydrokaempferide

Kaempferide was prepared from ω-benzoyloxy phloracetophenone, anisic anhydride and sodium anisate by the method of Heap and Robinson.[19] A solution of it (0·8 g) in 10% aqueous Na_2CO_3 (100 ml) was heated with stirring in a boiling water bath and sodium dithionite (20 g) added in small lots during a period of 10 min. There was vigorous evolution of H_2S and a yellow solid separated. The mixture was heated for 30 min, diluted with water (200 ml) and cooled in an ice bath. The mixture was then acidified with dilute HCl and kept aside at 0° for 4 hr; the unchanged kaempferide was filtered, and again reduced with sodium dithionite in the same way. The combined aqueous filtrate was extracted repeatedly with ether and the ether extract dried and distilled. The pale yellow residue was extracted with hot water and, on cooling, a colourless amorphous material separated. It crystallized from ethyl acetate–light petroleum as needles, m.p. 178–180° (Found: C, 62·8; H, 5·2; $C_{16}H_{14}O_6$ requires: C, 63·6; H, 4·6%). Light absorption: λ_{max}^{MeOH} 290 mμ; i.r. (Nujol): 1639 cm^{-1}. R_f values: 0·90 and 0·63 in "A" and "B". It gave a purplish-brown colour with alcoholic ferric chloride and a deep red colour with zinc and hydrochloric acid.

Racemization of Dihydrokaempferide (Natural)

The natural sample of dihydrokaempferide (0·1 g) was refluxed with 50% aqueous hydrochloric acid (25 ml) for 4 hr and filtered while hot. The filtrate on cooling deposited a pale yellow solid; on repeated crystallization from ethyl acetate–light petroleum, it separated as colourless prisms, m.p. 181–183° (previous sintering at 165°). Mixed melting point with the synthetic dihydrokaempferide was undepressed.

Methylation of Prudomestin

A mixture of prudomestin (40 mg) in dry acetone (50 ml), freshly ignited K_2CO_3 (0·3 g) and dimethyl sulphate (0·1 ml) was refluxed for 16 hr. The product crystallized from benzene–light petroleum as colourless prisms, m.p. 159–160° alone or when mixed with an authentic sample of (V) (Found: C, 64·6; H, 5·3; $C_{20}H_{20}O_7$ requires: C, 64·5; H, 5·4%).

[19] T. Heap and R. Robinson, *J. Chem. Soc.* 2336 (1926).

Ethylation of Prudomestin to its 7,3-Diethyl Ether (VI)

Prudomestin (48 mg) when heated under reflux for 6 hr in acetone (80 ml) with diethyl sulphate (0·034 ml) and anhydrous K_2CO_3 (0·3 g) gave its diethyl ether which crystallized from ethylacetate–light petroleum as small prisms (0·030 g), m.p. 121° (Found: C, 65·8; H, 6·0; $C_{21}H_{22}O_7$ requires: C, 65·3; H, 5·7%). Light absorption: λ_{max}^{MeOH} 272 mμ and 316 mμ; i.r. (Nujol): 1667 cm^{-1}. It gave a green colour with alcoholic ferric chloride.

Alkali Fission of Prudomestin Diethyl Ether (VI)

Prudomestin diethyl ether (18 mg) in alcoholic potash (50%; 3 ml) was refluxed for 2 hr. The solution was acidified and the solid that separated was taken up in ether and from the ether extract the acid component was extracted into aqueous sodium bicarbonate. The bicarbonate extract was acidified and shaken with ether. Evaporation of the ether left colourless needles of anisic acid, m.p. and mixed m.p. 181°; R_f value: 0·51 in butanol saturated with aqueous ammonia (using bromophenol blue as the developing agent).

ω-Benzoyloxy-2,4-dihydroxy-3,6-dimethoxy Acetophenone

A mixture of 1,4-dimethoxy-2,6-dibenzyloxy benzene[20] (8 g) and benzoyloxy acetonitrile (3·7 g) in dry ether (200 ml) was subjected to Hoesch acylation.[21] The resulting ketimine hydrochloride was hydrolysed by refluxing with 50% aqueous alcohol (200 ml) for 8 hr. The ketone, thus obtained crystallized from alcohol as colourless leaflets (3 g), m.p. 174°. Horowitz and Gentili[17] reported m.p. 178°.

3,7-Dihydroxy-5,8,4'-trimethoxyflavone (VIII)

A mixture of the above ketone (2 g), anisic anhydride (12 g) and sodium anisate (2 g) was heated between 160–170° in an oil bath for 5 hr. The resulting cake was dissolved in EtOH (50 ml) and then refluxed with 8% aqueous alcoholic KOH (100 ml) for 20 min. The alcohol was then removed under reduced pressure and the aqueous solution saturated with CO_2. The dark brown flavone that separated was converted into its acetate and crystallized from ethy acetate–light petroleum as small prisms, m.p. 154° (Found: C, 62·2; H, 4·6; $C_{22}H_{20}O_9$ requires: C, 61·7; H, 4·7%). Deacetylation of the acetate yielded the flavonol (VIII) (0·4 g), m.p. 279–280° and it was directly used for further experiments.

3,7-Diethoxy-5,8,4'-trimethoxyflavone

A mixture of the flavone (VIII) (0·2 g) in dry acetone (50 ml), diethyl sulphate (0·3 ml) and anhydrous potassium carbonate (0·6 g) was refluxed for 10 hr and the product was worked up as usual. The diethyl ether crystallized from aqueous acetone as needles melting at 83–85°; on keeping it became pasty.

Preparation of 5-Hydroxy-7,3-diethoxy-8,4'-dimethoxyflavone (VI)

A solution of the above flavone (0·1 g) in acetonitrile (30 ml) was refluxed with aluminium chloride (0·15 g) for 10 hr and then the acetonitrile removed under reduced pressure. The residue was heated with dilute hydrochloric acid for 20 min at 100°; the resulting flavone crystallized from ethyl acetate–light petroleum as small prisms (0·05 g), and mixed m.p. with the diethyl ether of prudomestin 120–121° (Found: C, 64·8; H, 6·2; $C_{21}H_{22}O_7$ requires: C, 65·3; H, 5·7%). Light absorption: λ_{max}^{MeOH} 272 mμ and 316 mμ; i.r. (Nujol): 1667 cm^{-1}. It gave a green colour with alcoholic ferric chloride.

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