227. *The Chemistry of Extractives from Hardwoods. Part XXXIII.*[1] *Extractives from* Melanorrhea *spp.* (*Rengas*).

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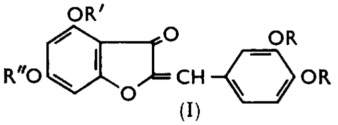
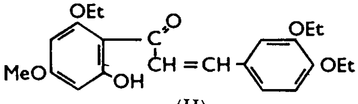
2-(3,4-Dihydroxybenzylidene)-4-hydroxy-6-methoxycoumaran-3-one (rengasin) and (±)-dihydroquercetin have been isolated from the heartwood of *Melanorrhea* spp. (rengas). The structure of the coumaranone was established by synthesis of the triethyl ether.

An ether extract of the ground heartwood of rengas (*Melanorrhea* spp.), a timber-producing tree of Malaya, was a mixture of an orange sticky solid and yellow crystals. The water-insoluble part of the former crystallised from aqueous methanol to give an orange-yellow compound (rengasin), $C_{15}H_9O_5{\cdot}OMe$. The formation of a trimethyl and triethyl ether and of a triacetate indicated three phenolic hydroxyl groups, and the colour reactions (ferric reaction green; alkali giving a reddish-purple solution) and the ultraviolet absorption ($\lambda_{max.}$ 403 mμ) suggested that the compound might well be a 2-benzylidene-trihydroxy-methoxycoumaran-3-one, although such aurones are rarely found in wood. The m. p. of the trimethyl ether was in good agreement with that of tetramethylaureusidin (I; $R = R' = R'' = Me$)[2] and the identity of the two compounds was confirmed by a mixed m. p. with synthetic material prepared by two methods.[2,3]



(I)



(II)

Rengasin gave a brown precipitate with chloropentamminecobalt(III) chloride, which suggested that both the oxygen substituents of the benzylidene group were unmethylated.[4] As methoxylation next to a carbonyl group in natural products is rarer than methoxylation in other positions it was probable that rengasin was the 6-methoxy-compound (I; $R = R' = H$, $R'' = Me$). This hypothesis was confirmed when a synthetic specimen of the ethyl ether (I; $R = R' = Et$, $R'' = Me$) proved identical with the ethyl ether of the natural product.

The synthesis was accomplished from 3′,4′,6-triethoxy-2-hydroxy-4-methoxychalcone (II), prepared by base-catalysed condensation of 3,4-diethoxybenzaldehyde and 6-ethoxy-2-hydroxy-4-methoxyacetophenone. The chalcone was converted into tri-*O*-ethyl-rengasin with hydrogen peroxide in the usual way. An alternative synthesis of the ether

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[1] Part XXXII, *J.*, 1961, 2714.

[2] Geissman and Siekel, *J. Amer. Chem. Soc.*, 1950, **72**, 5725.

[3] Dumont and Tambor, *Ber.*, 1910, **43**, 1969.

[4] Asahina, Asano, and Ueno, *Bull. Chem. Soc. Japan*, 1942, **17**, 104.

which involved partial methylation of the diethoxydihydroxycoumaranone (I; R = Et, R′ = R″ = H) failed at this stage.

The crystalline part of the ether extract of rengas gave, by crystallisation from water, a colourless compound which was shown by its properties and those of its tetramethyl ether and its tetramethyl ether acetate and penta-acetate to be (±)-dihydroquercetin. The structure of this compound, which we have also obtained from East African camphorwood (*Ocotea usambarensis*), was confirmed by dehydrogenation to quercetin and by mixed m. p. of the appropriate derivatives with synthetic dihydro-3′,4′,5,7-tetra-*O*-methylquercetin and its acetate. The synthetic compounds were prepared by cyclisation of 2,4′-dihydroxy-3′,4,6-trimethoxychalcone [5] under mild conditions with alkaline hydrogen peroxide, giving 3,4′-dihydroxy-3′,5,7-trimethoxyflavanone which was readily methylated to the dihydrotetra-*O*-methylquercetin.

EXPERIMENTAL

Ultraviolet absorptions refer to ethanolic solutions.

Extraction of Rengas.—The dry heartwood (3·1 kg.) was extracted for 18 hr. with boiling light petroleum (b. p. 60—80°), which removed *ca.* 5 g. of oil that gave a small yield of β-sitosterol after saponification. Subsequent extraction of the wood with boiling ether for 72 hr. gave an extract consisting of an orange gum (5—10 g.) and pale yellow crystals (0·16 g.), the latter being suspended in the solvent. The orange gum was triturated with cold water, and the insoluble fraction (1 g.) crystallised from aqueous methanol, to give *rengasin* as golden-yellow needles, m. p. 220° (decomp.) (Found, in a sample dried at 20°: C, 56·9; H, 4·6; OMe, 6·3. $C_{16}H_{12}O_6,2H_2O$ requires C, 57·1; H, 4·8; 1OMe, 9·2. Found, in a sample dried at 120°: C, 64·1; H, 4·3. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0%), $\lambda_{max.}$ 254 (ε 9900) and 403 mμ (ε 40,000).

Derivatives of Rengasin.—The yellow phenol with acetic anhydride and sodium acetate at 100° for 2 hr. afforded the *triacetate* as cream-coloured needles (from methanol), m. p. 209—210° (Found: C, 61·8; H, 4·2; OMe, 7·6; Ac, 32·9. $C_{22}H_{18}O_9$ requires C, 62·0; H, 4·3; 1OMe, 7·3; 3Ac, 30·3%), $\lambda_{max.}$ 313 (ε 18,000) and 385 mμ (ε 21,600). The trimethyl ether was prepared with dimethyl sulphate and potassium carbonate in boiling acetone for 18 hr. and crystallised in lemon-yellow needles, m. p. 169—170°, from ethanol (Found: C, 66·8; H, 5·5; OMe, 35·8. Calc. for $C_{19}H_{18}O_6$: C, 66·7; H, 5·3; 4OMe, 36·3%), $\lambda_{max.}$ 263 (ε 10,000) and 396 mμ (ε 30,000). Synthetic 2-(3,4-dimethoxybenzylidene)-4,6-dimethoxycoumaran-3-one had m. p. 169—170° undepressed by rengasin trimethyl ether, and its ultraviolet absorption was almost identical with that of the natural derivative. The *triethyl ether* was prepared with ethyl iodide and potassium carbonate in boiling acetone for 20 hr. and separated from ethanol as yellow needles, m. p. 150—152° (Found: C, 69·0; H, 5·9. $C_{22}H_{24}O_6$ requires C, 68·8; H, 6·3%).

3′,4′,6-*Triethoxy-2-hydroxy-4-methoxychalcone* (II).—50% Sodium hydroxide solution (0·5 c.c.) was added to a solution of 6-ethoxy-2-hydroxy-4-methoxyacetophenone (0·32 g.) and 3,4-diethoxybenzaldehyde (0·3 g.) in ethanol (10 c.c.), and the mixture was kept at 50° for 4 hr. An excess of dilute hydrochloric acid was then added and the precipitated *chalcone* crystallised from methanol as golden-yellow needles (0·33 g.), m. p. 138—139° (Found: C, 68·4; H, 6·7. $C_{22}H_{26}O_6$ requires C, 68·2; H, 6·8%).

2-(3,4-*Diethoxybenzylidene*)-4-*ethoxy*-6-*methoxycoumaran*-3-*one*.—Ice-cold 15% hydrogen peroxide (0·6 c.c.) was added dropwise to an ice-cold solution of the above chalcone (0·15 g.) in methanol (10 c.c.) containing aqueous 4N-sodium hydroxide (2 c.c.). After 18 hr. at 0° the yellow solid which had separated was crystallised from methanol to give the *coumaran-3-one* as yellow needles (0·1 g.), m. p. 152°, undepressed on admixture with tri-*O*-ethylrengasin (Found: C, 68·7; H, 6·3%).

2-(3,4-*Diethoxybenzylidene*)-4,6-*dihydroxycoumaran*-3-*one*.—20% Aqueous sodium hydroxide (2 c.c.) was added to a solution of 4,6-dihydroxycoumaran-3-one [6] (2 g.) and 3,4-diethoxybenzaldehyde in ethanol (20 c.c.). After 3 hr. at 40° the dark red solution was acidified with dilute hydrochloric acid, and the *dihydroxycoumaranone* (1·1 g.) crystallised from methanol as orange needles, m. p. 222—223° (Found: C, 67·0; H, 5·2. $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%), $\lambda_{max.}$ 255 (ε 8800) and 393 mμ (ε 30,800). Methylation of the phenol in acetone with methyl

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[5] Anand, Iyer, and Venkataraman, *Proc. Indian Acad. Sci.*, 1949, **29**, *A*, 203.

[6] Shriner and Grosser, *J. Amer. Chem. Soc.*, 1942, **64**, 383.

sulphate (1 equiv.) and potassium carbonate gave unchanged material as the only phenolic product. Diazomethane appeared to be without action on the phenol.

(±)-*Dihydroquercetin.*—The yellow crystals obtained in the extraction of rengas were repeatedly crystallised from water; (±)-dihydroquercetin was obtained with m. p. 226—227° (lit.,[7] 228—229°) (Found: C, 58·7; H, 4·0. Calc. for $C_{15}H_{12}O_7$: C, 59·2; H, 4·0%). The penta-acetate had m. p. 147—148° (lit.,[7] 153°) (Found: C, 57·9; H, 4·4. Calc. for $C_{25}H_{22}O_{12}$: C, 58·4; H, 4·3%); the tetramethyl ether had m. p. 166—167° (lit.,[7] 170°) (Found: C, 62·9; H, 5·7; OMe, 34·7. Calc. for $C_{19}H_{20}O_7$: C, 63·3; H, 5·7; 4OMe, 34·4%); and the tetramethyl ether acetate had m. p. 184—185° (lit.,[7] 186°) (Found: C, 62·4; H, 5·6. Calc. for $C_{21}H_{22}O_8$: C, 62·7; H, 5·5%).

3,4′-*Dihydroxy*-3′,5,7-*trimethoxyflavanone.*—15% Hydrogen peroxide (1·5 c.c.) was added to a solution of 2,4′-dihydroxy-3′,4,6-trimethoxychalcone[5] (0·8 g.) in 1% aqueous sodium hydroxide (40 c.c.). After 12 hr. at 0° the solution was acidified with dilute hydrochloric acid, and the precipitated *flavanone* (0·42 g.) crystallised from methanol as colourless needles, m. p. 184—186° (Found: C, 61·8; H, 5·3; OMe, 26·7. $C_{18}H_{18}O_7$ requires C, 62·4; H, 5·2; 3OMe, 26·9%). This compound with methyl sulphate in aqueous-alcoholic alkaline solution gave 3-hydroxy-3′,4′,5,7-tetramethoxyflavanone, m. p. 170—171° undepressed with the corresponding derivative of the natural product. The acetate of the synthetic tetramethyl ether had m. p. 183—184° undepressed by the tetramethyl ether acetate above.

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[7] Kondo, *J. Fac. Agric. Kyushi Univ.*, 1951, **10**, 79; *Chem. Abs.*, 1953, **47**, 4602.