459. *Flavonols from the Bark of* Melicope ternata. *Part I. The Isolation of Four New Flavonols, Meliternatin, Meliternin, Ternatin, and Wharangin.*

By Lindsay H. Briggs and R. H. Locker.

Four new flavonols, *meliternatin*, *meliternin*, *ternatin* and *wharangin*, of molecular formulæ $C_{19}H_{14}O_8$, $C_{20}H_{18}O_8$, $C_{19}H_{18}O_8$ and $C_{17}H_{12}O_8$ respectively, have been isolated from the bark of *Melicope ternata*. From degradative experiments definite formulæ, 3 : 5-dimethoxy-7 : 8 : 3′ : 4′-dimethylenedioxyflavone, 3 : 5 : 7 : 8-tetramethoxy-3′ : 4′-methylenedioxyflavone, and 5 : 4′-dihydroxy-3 : 7 : 8 : 3′-tetramethoxyflavone, are proposed for the first three compounds respectively, and a tentative formula is suggested for wharangin. Meliternatin and meliternin are unusual in being completely alkylated; the same two compounds and wharangin are unusual in containing methylenedioxy-groups, and meliternatin is unique in containing two such groups.

Melicope ternata (genus *Melicope*, order *Rutaceae*, Maori name "Wharangi") is a small tree, 12—20 feet high, endemic to and occurring in both Islands of New Zealand, with other species in Australia, the Pacific Islands, and tropical Asia. The inner bark is bright yellow, aromatic, and bitter to the taste.

Following the isolation of coloured alkaloids, melicopine, melicopidine, and melicopicine from Australian *Melicope* species (Hughes, Lahey, Price, and Webb, *Nature*, 1948, **162**, 223), an examination of the bark of *Melicope ternata* first revealed the presence of two basic constituents which gave precipitates with the usual alkaloidal reagents and crystalline salts with acids. The compounds, however, contained no nitrogen and proved to be completely

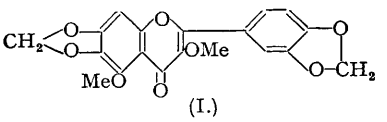
alkylated hydroxyflavones. Their basic properties were then utilised in the following method of extraction.

The dried bark was first extracted to completion with acetone, the acetone removed, and the residue completely extracted with trichloroethylene. Concentrated hydrochloric acid removed the completely alkylated flavones which were precipitated on dilution with water and separated by fractional crystallisation into flavonol *A*, $C_{19}H_{14}O_8$, and flavonol *B*, $C_{20}H_{18}O_8$. The trichloroethylene extract was then extracted successively with sodium hydrogen carbonate, sodium carbonate, and sodium hydroxide solution, and these were acidified. The hydrogen carbonate extract gave no crystalline material, the carbonate extract gave a third flavonol, flavonol *C*, $C_{17}H_{12}O_8$, purified by crystallisation, whilst the hydroxide solution furnished a mixture from which a fourth flavonol, flavonol *D*, $C_{19}H_{18}O_8$, and a crystalline non-flavone *compound*, $C_{16}H_{16}O_4$ (?), could be separated by fractional crystallisation. All four flavonols proved to be new compounds for which the names *meliternatin*, *meliternin*, *wharangin*, and *ternatin* are proposed for *A*, *B*, *C*, and *D*, respectively.

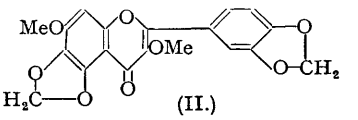
Meliternatin, $C_{19}H_{14}O_8$.—Meliternatin gives highly coloured solutions in concentrated mineral acids (from which it is precipitated on dilution), a crystalline hydrochloride, perchlorate, picrate, and picrolonate, and a precipitate with the usual alkaloidal reagents. It is insoluble in sodium hydroxide solution. It gives no colour with ferric chloride but a positive test for a methylenedioxy-group. Two methoxyl groups are present (Zeisel).

Reduction with magnesium and hydrochloric acid, as well as with sodium amalgam followed by acidification, gives the same salmon-pink colour. Asahina and Inubuse (*Ber.*, 1928, **61**, *B*, 1646) first found that flavones may be reduced to anthocyanidins only in alkaline solution, and flavonols only in acid solution, but flavanones in both acid and alkaline solution. This conclusion was later modified by the discovery (*Ber.*, 1929, **62**, *B*, 1256) that quercetin pentamethyl ether and rutin (quercetin-3-rhamnoglucoside) could be reduced in alkaline solution. We have extended this reaction and found that flavonols with a methoxyl group at $C_{(3)}$, in contrast with those with a free hydroxyl group at $C_{(3)}$, are reduced by sodium amalgam. The above reactions indicate that meliternatin is a flavone, and the molecular formula may then be accommodated by the presence of two methoxyl groups—one of them at $C_{(3)}$—and two methylenedioxy-groups.

Dealkylation with hydriodic acid afforded quercetagetin (3 : 5 : 6 : 7 : 3′ : 4′-hexahydroxyflavone), indicating two possibilities (I) and (II) for meliternatin. However, norwogonin dimethyl ether (7-hydroxy-5 : 8-dimethoxyflavone) and 7-hydroxy-5 : 8 : 4′-trimethoxyflavone are demethylated to baicalein (5 : 6 : 7-trihydroxyflavone) and scutellarein (5 : 6 : 7 : 4′-tetrahydroxyflavone), respectively, equivalent to the rearrangement of a 5 : 8- to a 5 : 6-configuration. Similarly 5 : 8-dimethoxyflavone is demethylated to 5 : 6-dihydroxyflavone with hydrobromic acid, but aluminium chloride as a dealkylating agent is free from this complication (for a summary, see Shah, Mehta, and Wheeler, *J.*, 1938, 1555). When aluminium chloride was used in this case an aluminium lake was produced from which, however, the aluminium could not be removed. The alternative, therefore, that meliternatin is a 5 : 7 : 8-derivative still remains for which there is only one possibility (III).

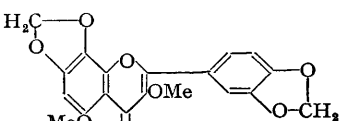


(I.)

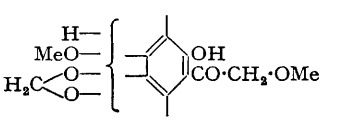


(II.)

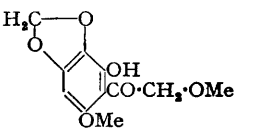
Hydrolysis of meliternatin with alcoholic potassium hydroxide yielded four products: piperonylic acid, which confirmed the structure of the side phenyl group, and three phenols. The structure of two of them adds little to the solution of the problem, but the third, $C_{11}H_{12}O_6$, obtained in greatest amount contains two methoxyl groups and a methylenedioxy-group and corresponds to the expected *compound* (IV).



(III.)



(IV.)



(V.)

The rigidly purified phenol gives a positive test with 2 : 6-dibromoquinonechloroimide

(Gibbs, *J. Biol. Chem.*, 1927, **72**, 649) indicating a free position *para* to the phenolic group. It must therefore have the structure (V), and the meliternatin structure must be (III).

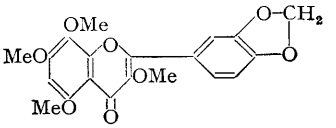
Meliternin, $C_{20}H_{18}O_8$.—In its general properties meliternin reacts similarly to meliternatin but contains four methoxyl groups, the methylenedioxy-test again being positive. All the oxygen atoms are thus accounted for. Demethylation with hydriodic acid yielded gossypetin (3 : 5 : 7 : 8 : 3′ : 4′-hexahydroxyflavone). In this case the question of group migration does not occur, as rearrangements from a 5 : 6- to a 5 : 8-configuration have not been recorded. Hydrolysis with alcoholic potassium hydroxide gave piperonylic acid, establishing the structure of the side phenyl group and that of meliternin as (VI), which has now been confirmed by synthesis (succeeding paper).

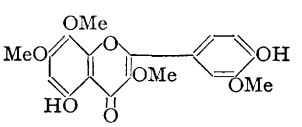
Ternatin, $C_{19}H_{18}O_8$.—Ternatin gives bright-yellow solutions with concentrated mineral acids but, although it is only slightly soluble in concentrated hydrochloric acid, its solution will give precipitates with alkaloidal reagents. It dissolves in aqueous sodium hydroxide but not in carbonate solution. It gives a green coloration with ferric chloride but the methylenedioxy-test is negative. It is reduced in acid or alkaline solution giving a strong reddish-violet colour, indicating a flavone with a methoxyl group at $C_{(3)}$. Four methoxyl groups are present, indicating a dihydroxy-tetramethoxy-flavone.

Demethylation with hydriodic acid gave quercetagetin, but here, as in the case of meliternatin, rearrangement may have occurred during the reaction. Methylation, however, with methyl sulphate and potassium carbonate afforded gossypetin hexamethyl ether where the question of rearrangement does not arise. There remains to be decided only the position of the free phenolic groups.

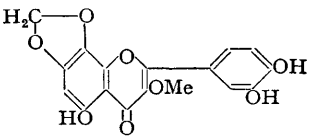
Hydrolysis of the diethyl ether with alcoholic potassium hydroxide yielded the ethyl ether of vanillic acid, proving the position of one free hydroxyl group at position 4′. Since ternatin has dyeing properties on mordanted wool it must have a free hydroxyl group at $C_{(3)}$ or $C_{(5)}$. Since the colour produced on alkaline reduction indicates a methoxyl group at $C_{(3)}$, the remaining hydroxyl group must be at $C_{(5)}$, and ternatin may be formulated as (VII). This has been confirmed by synthesis (forthcoming communication), and is also in harmony with the observation that in flavones containing hydroxy-groups in the 5 and 6, 7, or 8 positions which are partly methylated the position 5 is invariably unmethylated.

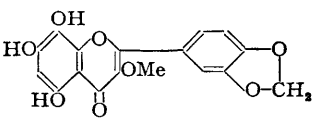
Wharangin, $C_{17}H_{12}O_8$.—Only 60 mg. of this compound were isolated and our constitutional deductions are based solely on colour reactions. This is the least basic compound of the series, being insoluble in concentrated hydrochloric acid, but dissolving in concentrated sulphuric acid to an intense yellowish-orange solution. On the other hand, it is more acidic than ternatin, dissolving in sodium carbonate as well as hydroxide solution. It gives a greenish-brown colour with ferric chloride, and the methylenedioxy-test is also positive. A strong salmon-pink colour is produced on acid or alkaline reduction, which indicates a flavonol methylated in position 3, this being the only methoxyl group shown as present by a Zeisel determination. Wharangin corresponds, therefore, to a trihydroxy-methoxy-methylenedioxy-flavone.

(VI.) 

 (VII.)

The three hydroxy-groups are not in vicinal position since wharangin does not give the Bargellini test (*Gazzetta*, 1919, **49**, ii, 47) characteristic of 5 : 6 : 7-trihydroxyflavones. Seshadri and Rao (*Proc. Ind. Acad. Sci.*, 1943, **17**, *A*, 20) have extended this reaction by reporting that norkanugin (3 : 7 : 3′ : 4′ : 5′-pentahydroxyflavone) also gives the test, whilst we have observed that anthragallol and areolatin (1 : 5 : 6 : 7-tetrahydroxy-2-methylanthraquinone) (*J.*, 1948, 599, 990) also gives positive tests.

(VIII.) 

 (IX.)

If on phytochemical grounds the same position is assumed for the oxygen atoms as in the three compounds already discussed, two formulæ (VIII) and (IX) are possible for wharangin.

A compound (IX) has been synthesised (succeeding paper), which does not agree in its properties with wharangin, for which we therefore suggest tentatively the formula (VIII).

It is interesting to note that of the four other completely alkylated flavones three of these, nobiletin (Tseng, *J.*, 1938, 1003; Robinson and Tseng, *ibid.*, 1938, 1004), tangeretin (Nelson, *J. Amer. Chem. Soc.*, 1934, **56**, 1392; Goldsworthy and Robinson, *J.*, 1937, 46) and aurantin (Patnayak, Rangawami, and Seshadri, *Proc. Ind. Acad. Sci.*, 1942, **16**, *A*, 10) occur in citrus species of the *Rutaceae*, of which *Melicope ternata* is a member, while the fourth, kanugin, from *Pongamia glabra* (*Leguminosae*) (Rao and Seshadri, *Proc. Ind. Acad. Sci.*, 1946, **23**, *A*, 147) is the only other naturally occurring flavone containing a methylenedioxy-group. ψ-Baptigenin, an *iso*flavone (Späth and Lederer, *Ber.*, 1930, **63**, *B*, 743), also contains a methylenedioxy-group. Meliternatin is unique in containing two such groups.

Experimental.

(M. p.s are corrected.)

Isolation of the Flavonols.—The bark was collected from mature trees at Papa Aroha, Coromandel. The air-dried powdered bark (2 kg.) was continuously extracted with acetone for 96 hours. After removal of the acetone, the residue was taken up in trichloroethylene, which was decanted later from a tarry deposit which settled out. The solution was then extracted with concentrated hydrochloric acid (10 × 200 c.c.), which next day was decanted from impurities. After dilution with 2 volumes of water, the acid layer was shaken with chloroform and separated from a further tarry deposit formed on dilution. The chloroform extract, a thick black tar, was dissolved in boiling dioxan and diluted with about its own volume of water. A black oil, which formed immediately, was removed by decantation and, from the solvent, a solid separated on cooling, contaminated with some oil. Fractional crystallisation of the solid from aqueous dioxan and then from alcohol afforded two products, flavonol *A* (*meliternatin*) and flavonol *B* (*meliternin*). The oil precipitated from the original dioxan–water mixture also yielded further material on trituration with alcohol. The total yield of meliternatin was 5·5 g. and that of meliternin 1 g.

The trichloroethylene layer was then extracted successively with saturated sodium hydrogen carbonate solution (5 × 500 c.c.), six times with almost saturated sodium carbonate solution and three times with 10% sodium hydroxide solution, and all the extracts were acidified. The oil separating from the hydrogen carbonate extract was dissolved in alcohol but no crystalline material could be obtained. The brown product from the carbonate extract yielded flavonol *C* (*wharangin*) (60 mg.) after crystallisation from alcohol and then from acetone. The product from the first hydroxide extract crystallised from alcohol to give flavonol *D* (*ternatin*), that from the third extract, compound *E*. All the products gave alternate crops of *D* and *E* on fractional crystallisation (yield of *D* and *E*, 260 and 160 mg., respectively).

Meliternatin could also be obtained readily from the bark by extraction first with boiling water and then with light petroleum (b. p. 40—60°) and working up the petroleum extract with acetone.

Meliternatin.—Meliternatin crystallises from alcohol in colourless needles, m. p. 198—198·5° (Found: C, 61·2; H, 4·0; OMe, 16·3. $C_{19}H_{14}O_8$ requires C, 61·6; H, 3·8; 2OMe, 16·8%). It is insoluble in hot or cold water and light petroleum, almost insoluble in ether, and soluble in the other usual organic solvents. A solution in concentrated sulphuric acid with a drop of 5% alcoholic gallic acid became yellowish-brown, but intense green overnight. The same test with phloroglucinol became first orange and overnight a clear orange-red, very sluggish tests compared with those of piperonal.

The hydrochloride was formed in bright yellow needles when a solution of meliternatin in concentrated hydrochloric acid was shaken or when hydrogen chloride was passed into its solution in benzene. The hydrochloride decomposes slowly when kept but rapidly when heated or when placed in a vacuum, reverting to meliternatin. When treated with hot perchloric acid it changes to orange-yellow but does not dissolve. The perchlorate formed needles, m. p. 223°, when purified from absolute alcohol. The picrate, prepared as for a base in alcohol solution, formed rosettes of slender yellow needles, m. p. ca. 90° (decomp.). The picrolonate, similarly prepared, formed mustard-coloured prisms, m. p. 127·5° (decomp.).

Dealkylation of Meliternatin to Quercetagetin.—Meliternatin (200 mg.) was heated for 2 hours at 150—155° with hydriodic acid (6 c.c., *d* 1·7) and phenol (3 c.c.) in an atmosphere of carbon dioxide. The yellow precipitate (160 mg.) formed on pouring the mixture into water, after repeated crystallisation from aqueous alcohol (2 : 1), formed clusters of mustard-coloured needles, m. p. 323° (decomp.), undepressed by an authentic specimen of quercetagetin, m. p. 324—325° (decomp.). The acetate, prepared by heating the dealkylated material (40 mg.) with acetic anhydride (0·2 c.c.) and pyridine (1 drop), was precipitated with and crystallised from alcohol, forming long, colourless, silky needles, m. p. 212—213°, undepressed by an authentic specimen of quercetagetin hexa-acetate of the same m. p.

Hydrolysis of Meliternatin.—Meliternatin (1 g.) dissolved in slightly diluted alcohol (35 c.c.) and potassium hydroxide (2 g.) was heated on the water-bath for 7 hours. On cooling, yellow needles of a potassium salt (product I, 70 mg.), separated and were filtered off. Carbon dioxide was bubbled through the filtrate until acid to phenolphthalein. The brown solid (product II; 420 mg.) which separated was filtered off. The filtrate, on acidification with hydrochloric acid, gave a colourless precipitate (product III; 430 mg.).

Product I, on acidification with dilute hydrochloric acid, gave a colourless substance, crystallising from acetone in pale cream, silky needles, m. p. 258—259° (26 mg.) [Found: C, 60·1; H, 3·7; OMe, 8·1. $C_{11}H_8O_5$ (?) requires C, 60·0; H, 3·6; OMe, 14·1%]. It gave a greenish-brown colour with ferric chloride, an intense green colour overnight with gallic acid in the methylenedioxy-test, but no reaction

with 2 : 6-dibromoquinonechloroimide (this may have been due to its insolubility in the buffer at pH 9·2). The composition of this compound does not correspond with any of the expected products.

Product II could not be induced to crystallise, but a portion readily sublimed at 100—120° in a high vacuum. The bright yellow, crystalline sublimate (250 mg.) then crystallised from alcohol in yellow prisms, m. p. 138·5—139·5° (mg.) (Found: C, 55·4; H, 5·65; OMe, 25·4. $C_{11}H_{12}O_8$ requires C, 55·0; H, 5·0; 2OMe, 25·8%). This material gave a dark green colour with ferric chloride, and slowly a strong green colour in the methylenedioxy-test with gallic acid. A portion was thrice crystallised, twice from charcoal, and the cream-coloured prisms, m. p. 142—144°, then gave a strong violet colour in a few minutes with an aqueous suspension of 2 : 6-dibromoquinonechloroimide buffered at pH 9·2. These properties correspond with the expected structure of 2-*hydroxy*-6 : *ω*-*dimethoxy*-3 : 4-*methylenedioxy*-*acetophenone*.

The residue from the sublimation was also resistant to crystallisation, but could readily be crystallised as its sodium salt from 10% sodium hydroxide solution. The yellow needles so obtained were dissolved in hot water, and the colourless product obtained after acidification was twice crystallised from alcohol to give long, colourless needles, m. p. 194—195° (33 mg.) [Found: C, 61·9; H, 4·7; OMe, 11·6. $C_{10}H_{10}O_4$ (?) requires C, 61·8; H, 5·1; 1OMe, 16·0%]. This material is soluble in sodium carbonate solution to give a yellow solution, and it gives no colour with ferric chloride and slowly an intense green colour in the methylenedioxy-test. The composition of this compound does not correspond with any of the expected products.

Product III was crystallised from alcohol, sublimed at 210° at atmospheric pressure, and recrystallised from the same solvent. The m. p. (230—231·5°) of the colourless prisms was undepressed by an authentic specimen of piperonylic acid.

Meliternin.—Meliternin crystallises from alcohol in colourless prisms, m. p. 185·5—186° (Found: C, 61·65; H, 4·6; OMe, 35·0. $C_{20}H_{18}O_8$ requires C, 62·2; H, 4·7; 4OMe, 32·1%). It is insoluble in water, moderately soluble in alcohol and acetone, and soluble in chloroform, benzene, and dioxan. It gave only a slight green colour overnight in the methylenedioxy-test with gallic acid and an orange-red colour in the same test with phloroglucinol, but a reddish-brown colour was produced with concentrated sulphuric acid alone in the same period.

An orange amorphous hydrochloride formed when a solution of meliternin in benzene was treated with dry hydrogen chloride. Orange-red needles of a sulphate separated from an absolute alcoholic solution of meliternin when treated with concentrated sulphuric acid. Both salts decomposed immediately in contact with water and when kept. In concentrated hydrochloric acid meliternin gave coloured precipitates with the usual alkaloidal reagents. Reduction of an alcoholic solution with magnesium and hydrochloric acid or with sodium amalgam followed by acidification both gave an intense reddish-violet colour.

Dealkylation of Meliternin to Gossypetin.—Meliternin (100 mg.) was heated for 3 hours at 150—160° with hydriodic acid (3 c.c.; *d* 1·7) and phenol (1·5 c.c.). The product formed on pouring the mixture into water and crystallised repeatedly from aqueous alcohol (1 : 1) formed yellow needles, m. p. 304—305° (33 mg.). The dealkylated product was acetylated with excess of acetic anhydride and a drop of perchloric acid (60%) at room temperature. The product formed on pouring the mixture into water separated, after repeated crystallisation from methyl alcohol, in colourless needles, m. p. 229·5—231·5°. Perkin (*J.*, 1913, **103**, 650) records m. p. 228—230° for gossypetin hexa-acetate and Baker, Nodzu, and Robinson (*ibid.*, 1929, 74), m. p. 229—230°.

A small amount of this acetate was hydrolysed by dissolving it in concentrated sulphuric acid, setting the mixture aside for 10 minutes at room temperature and pouring it into water. The purified material then had m. p. 313—314°, undepressed by an authentic specimen of gossypetin. A solution of this material in a few drops of alcohol, added to a buffer of pH 9·8, rapidly changed from green to blue, a characteristic reaction of gossypetin and also of herbacetin and hibiscetin, all 3 : 5 : 7 : 8-polyhydroxyflavones.

Hydrolysis of Meliternin.—A solution of meliternin (90 mg.) and potassium hydroxide (200 mg.) in 80% alcohol (2 c.c.) was heated on the water-bath for 8 hours. The alcohol was removed by distillation, the residue completely dissolved in water (4 c.c.), and carbon dioxide bubbled through the solution until it was acid to phenolphthalein. Extraction with ether afforded a small amount of yellow needles, but on attempted purification only a red oil was obtained. The residual aqueous solution was acidified and the precipitate (33 mg.), after repeated crystallisation from alcohol, formed colourless prisms, m. p 230—231·5°, undepressed by piperonylic acid.

Ternatin.—*Ternatin* crystallises from alcohol in yellow, silky needles, m. p. 210—210·5° (Found: C, 60·5; H, 4·9; OMe, 33·2. $C_{19}H_{18}O_8$ requires C, 61·0; H, 4·8; 4OMe, 33·2%). It is insoluble in water and light petroleum, moderately soluble in alcohol, and soluble in acetone.

An acetate of ternatin, obtained by acetic anhydride–pyridine, formed, after crystallisation from alcohol, pale cream-coloured needles, m. p. 165—166°, unreactive to ferric chloride solution. The acetate was photosensitive, however, and became orange on exposure to light.

Demethylation of Ternatin to Quercetagetin.—Ternatin (61 mg.) was heated for 3 hours at 150—160° with hydriodic acid (3 c.c.; *d* 1·7) and phenol (1·5 c.c.) in an atmosphere of carbon dioxide. The yellow precipitate (40 mg.), formed on pouring the mixture into water, crystallised from aqueous alcohol in yellow needles, m. p. *ca.* 306° (decomp.). The dealkylated product (21 mg.) was acetylated with acetic anhydride (0·2 c.c.) and 60% perchloric acid (1 drop) at room temperature for 2 hours. The product formed on pouring into water was crystallised successively from ethyl acetate and methyl alcohol, forming colourless prisms, m. p. 207—210°, undepressed by quercetagetin hexa-acetate.

Methylation of Ternatin to Gossypetin Hexamethyl Ether.—A solution of ternatin (60 mg.) in dry acetone (5 c.c.) was heated under reflux with anhydrous potassium carbonate (1 g.) and methyl sulphate (0·1 c.c.) for 6 hours. The acetone solution was filtered and concentrated to *ca.* 1 c.c. The colourless prisms separating on cooling (33 mg.) had, after two crystallisations from alcohol, m. p. 169—170°, undepressed by gossypetin hexamethyl ether, m. p. 170—171°.

Ternatin Diethyl Ether and its Hydrolysis.—Ternatin (100 mg.), dissolved in absolute alcohol (3 c.c.),

was ethylated by being heated under reflux with ethyl iodide (0·46 c.c.), potassium hydroxide (170 mg.) being added gradually during 6 hours. After a further hour's heating the excess of alcohol and ethyl iodide was distilled off and the product was repeatedly crystallised from alcohol to form almost colourless needles, m. p. 231·5—235·5° (46 mg.), giving no colour with ferric chloride.

A solution of ternatin diethyl ether (45 mg.) in 80% alcohol (2 c.c.) was heated with potassium hydroxide (340 mg.) for 6 hours. The alcohol was almost completely removed and carbon dioxide passed into an aqueous solution (5 c.c.) of the residue until it was acid to phenolphthalein. Brown needles of a potassium salt (12 mg.) separated, from which the free compound was liberated by dissolution in hot water and acidification with hydrochloric acid, whereupon long, fine, almost colourless needles separated, m. p. 150—151°, giving a brown colour with ferric chloride. This should be the unknown compound, 2-hydroxy-3 : 4 : ω-trimethoxy-6-ethoxyacetophenone but there was insufficient for analysis.

The residual aqueous solution was then acidified with hydrochloric acid. The product separating (7 mg.), after crystallisation from alcohol, formed colourless needles, m. p. 197—198°, undepressed by a synthetic sample of *O*-ethylvanillic acid of the same m. p.

Dyeing Properites of Ternatin.—A sample of wool mordanted with potassium dichromate and tannic acid was well washed with hot water and dyed by boiling it with a suspension of ternatin (*ca.* 2 mg.) in water (3 c.c.) for 10 minutes. The wool was dyed a pale mustard colour, unchanged after boiling with fresh water for 20 minutes.

Wharangin.—Wharangin crystallises from acetone in yellow needles, m. p. 277—278° (Found : C, 59·2; H, 3·8; OMe, 6·8. $C_{17}H_{12}O_8$ requires C, 59·3; H, 3·5; 1OMe, 9·0%). It is insoluble in water and light petroleum, and sparingly soluble in methyl and ethyl alcohol and acetone.

Compound E.—This compound crystallises from alcohol in colourless prisms or plates, m. p. 133·5—134° [Found : C, 70·2; H, 5·5; OMe, 11·8, 10·7%; *M*, 259, 288 (ebullioscopic in benzene). $C_{16}H_{16}O_4$ (?) requires C, 70·6; H, 5·9; 1OMe, 11·4% : *M*, 272]. It is insoluble in water and moderately soluble in alcohol. It dissolves in concentrated sulphuric acid with an orange solution but is insoluble in concentrated hydrochloric acid. Despite the fact that it was obtained by extraction with sodium hydroxide solution the purified material dissolves with the greatest difficulty in 10% hot or cold solution, giving a pale yellow solution. A faintly alkaline alcoholic solution shows a pale green fluorescence. The ferric chloride reaction is negative but the methylenedioxy-test with gallic acid gives an intense green colour overnight. No flavone test is given by acid or alkaline reducing agents, bromine in chloroform is decolorised immediately, whilst Brady's reagent gives no precipitate.

Absorption Spectra.—The absorption spectra of the new flavonols, compound *E*, and gossypetin hexamethyl ether and quercetagetin hexamethyl ether for comparison, were measured in *ca.* N/20,000 alcoholic solution in a Beckman spectrophotometer, Model DU, peaks being obtained as follows :

Compound.	λ.	log ε.	λ.	log ε.	λ.	log ε.
Meliternatin	249	4·24	269 *	4·11	336	4·40
Meliternin	253	4·33	272	4·24	350	4·27
Ternatin	258	4·31	273	4·28	368	4·26
Wharangin	261	4·32	273	4·27	377	4·27
Gossypetin hexamethyl ether	253	4·34	271	4·33	350	4·33
Quercetagetin hexamethyl ether	256	4·37	267 *	4·31	349	4·33
Compound *E*	227	4·30	269	4·34	346	4·07

* Points of inflexion.

The analyses are by Drs. Weiler and Strauss, Oxford, and Mr. R. N. Seelye of this department. We are indebted to the Chemical Society, the Royal Society of New Zealand, the Australian and New Zealand Association for the Advancement of Science, and the Research Grants Committee of the University of New Zealand for grants, and for a Research Scholarship to one of us (R. H. L.), to Dr. T. J. Sprott for measurement of some of the absorption spectra, and especially to Professor T. R. Seshadri for samples of quercetagetin and gossypetin derivatives and information concerning their colour reactions.

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