518. *The Occurrence of Dihydrokæmpferol in* Nothofagus *Species.*

By N. F. Janes and J. W. W. Morgan.

The absolute configuration of (+)-dihydrokæmpferol, a constituent of coigue (*Nothofagus spp.*), has been determined by catalytic reduction of its trimethyl ether in acetic acid to (+)afzelechin trimethyl ether. Similar reduction in ethanol or by lithium aluminium hydride or sodium borohydride affords *trans*-5,7,4′-trimethoxyflavan-3,4-diol. Engelitin and isoengelitin, two stereoisomeric dihydrokæmpferol 3-L-rhamnosides, have been isolated from rauli (*N. procera*).

Timbers of the *Nothofagus* species are used commercially as substitutes for beech. Two members of this species commonly imported from Chile are coigue (*N. dombeyi*) and rauli (*N. procera*), and their extractives form the subject of this communication.

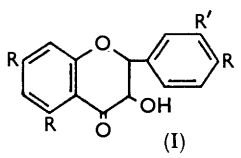
Extraction of the shredded heartwood of coigue by light petroleum and then ether yielded only small amounts of a yellow wax (0·5%) from which ferulic acid (0·03%) was obtained after alkaline hydrolysis. Subsequent extraction with acetone gave ellagic acid (0·3%) and (+)-dihydrokæmpferol (I; R = OH, R′ = H) (1·1%), readily separated by virtue of the solubility of the latter in hot water. Pew [1] isolated (+)-dihydrokæmpferol from coigue together with naringenin, by extraction with cold aqueous methanol, but we could not find the latter in any of our extracts. Botanical examination of the timber alone does not allow coigue to be described unambiguously as *N. dombeyi*, but the present sample has been identified as a member of the *Nothofagus* species, probably *N. dombeyi* or *N. antarctica*. (+)-Dihydrokæmpferol has been isolated from a number of other timbers, including katsura (*Cercidiphyllum japonicum*),[2,3] European larch (*Larix decidua*),[3] *Eucalyptus calophylla*,[4] and doussie (*Afzelia* spp.).[5,6]

The (+)-dihydrokæmpferol obtained in this work was characterised by oxidation to kæmpferol (II; R = OH, R′ = H) [1] and as derivatives. Acetylation of the active form by Brewerton's method [7] affords a (+)-3,7,4′-triacetate, m. p. 135°, but if the (+)-dihydrokæmpferol is first racemised by boiling acid a (±)-3,7,4′-triacetate, m. p. 171—172°, is obtained. A mixture of the active and the racemic acetate melts at an intermediate temperature, but the two compounds were proved to be structurally alike by their coincident infrared spectra. The trimethyl ether is very sensitive to alkali,[8] being converted by 5% alcoholic potassium hydroxide at room temperature into kæmpferol 5,7,4′-trimethyl ether in 85% yield in 3 minutes. Hergert, Coad, and Logan [9] observed that similar brief treatment of dihydroquercetin 5,7,3′,4′-tetramethyl ether (I; R = R′ = OMe) gives the coumaranone (III) but that boiling it with aqueous potassium hydroxide for 15 minutes is necessary to obtain quercetin tetramethyl ether (II; R = R′ = OMe).

The absolute configuration of (+)-dihydrokæmpferol has been established by the method used by Clark-Lewis and Korytnyk [10] for (+)-dihydroquercetin—its tetramethyl ether was reduced to (+)-catechin tetramethyl ether of known absolute configuration. The absolute configuration of (+)-catechin (IV; R = R′ = OH) has been deduced by Freudenberg,[11] and by Birch, Clark-Lewis, and Robertson [12] (in spite of objections by Brown and

[1] Pew, *J. Amer. Chem. Soc.*, 1948, **70**, 3031.
[2] Uoda, Fukushima, and Kondo, *J. Agr. Chem. Soc. Japan*, 1943, **19**, 467; *Chem. Abs.*, 1948, **42**, 5088; 1951, 9136.
[3] Gripenberg, *Acta Chem. Scand.*, 1952, **6**, 1152.
[4] Hillis, *Austral. J. Sci. Res.*, 1952, *A*, **5**, 379.
[5] King and Acheson, *J.*, 1950, 168.
[6] King, Clark-Lewis, and Forbes, *J.*, 1955, 2948.
[7] Brewerton, *New Zealand J. Sci. Technol.*, 1957, **38**, *B*, 697.
[8] Tominaga, *J. Pharm. Soc. Japan*, 1953, **73**, 1175; *Chem. Abs.*, 1954, 12,741.
[9] Hergert, Coad, and Logan, *J. Org. Chem.*, 1956, **21**, 304.
[10] Clark-Lewis and Korytnyk, *Chem. and Ind.*, 1957, 1418; *J.*, 1958, 2367.
[11] Freudenberg, *Sci. Proc. Royal Dublin Soc.*, 1956, **27**, 153.
[12] Birch, Clark-Lewis, and Robertson, *J.*, 1957, 3586.

Somerfield [13] which were later invalidated [14]); in addition, the absolute configuration of (+)-catechin has been established by Hardegger, Gempeler, and Zust [15] using a method independent of the relation between catechin and epicatechin.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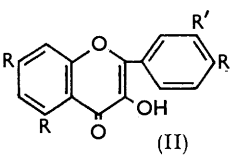
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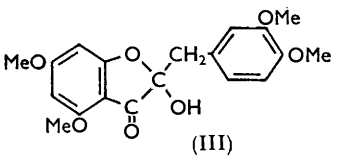
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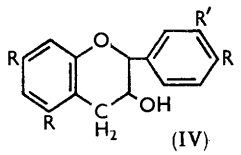
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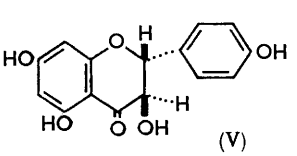
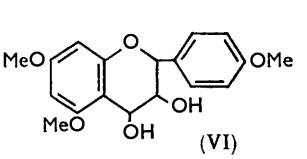

(V)


(VI)

Hydrogenation of (+)-dihydrokæmpferol 5,7,4′-trimethyl ether over a platinum catalyst in acetic acid gives a 5,7,4′-trimethoxyflavan-3-ol. A comparison of the properties of this compound, its acetate, and its toluene-*p*-sulphonate with those of the corresponding derivatives of (+)-catechin, (−)-epicatechin, and (−)-epiafzelechin [6] (see Table) establishes that it is (+)afzelechin 5,7,4′-trimethyl ether (IV; R = OMe, R′ = H). It has been shown that compounds of the catechin series have the *trans*-configuration, and those of the epicatechin series the *cis*-configuration at positions 2 and 3 [6,16] and it follows that the new (+)-afzelechin trimethyl ether has the *trans*-structure. Accordingly the (+)-dihydrokæmpferol from which this compound was derived must have the *trans*-configuration, which agrees with the generalisation of Mahesh and Seshadri [17] concerning the structure of the naturally occurring dihydroflavonols. This assignment allows the further conclusion that (+)-dihydrokæmpferol has the same absolute configuration (V) as (+)-catechin, and can be described as (2*R*,3*R*)-3,5,7,4′-tetrahydroxy-4-flavanone.[18]

In the reduction of (+)-dihydrokæmpferol trimethyl ether the absorption of hydrogen does not stop at the theoretical 2 mols., and the optimum yield of (+)-afzelechin trimethyl ether is obtained by stopping the reaction after 3 mols. of hydrogen have been taken up. In ethanol, however, only 1 mol. of hydrogen reacts and the product is a 5,7,4′-trimethoxyflavan-3,4-diol (VI), which can be obtained also by use of lithium aluminium hydride or sodium borohydride. The compound gave a red colour with acid characteristic of a flavan-3,4-diol but failed to give an isopropylidene derivative or a cyclic carbonate under conditions where other *cis*-flavan-3,4-diols have given these derivatives.[19,20] Moreover the diol did not give a borate complex,[21] whence it must be concluded that it is a *trans*-3,4-diol. As the *trans*-disposition of the 2-aryl and the 3-hydroxyl group has already been demonstrated the configuration of the trimethoxyflavandiol is completely known, and of the two possible conformations for this compound (2*eq*, 3*eq*, 4*eq*, and 2*ax*, 3*ax*, 4*ax*) the former is preferred.

The formation of the *trans*-3,4-diol (3*eq*, 4*eq*) by reduction with lithium aluminium hydride and sodium borohydride is expected, as such reductions of an unhindered carbonyl

[13] Brown and Somerfield, *Proc. Chem. Soc.*, 1958, 236.
[14] Clark-Lewis, *Proc. Chem. Soc.*, 1959, 388.
[15] Hardegger, Gempeler, and Zust, *Helv. Chim. Acta*, 1957, **40**, 1819.
[16] Whalley, "The Stereochemistry of the Chromans and Related Compounds," Symposium on Vegetable Tannins, Cambridge, Society of Leather Trades' Chemists, Croydon, 1956, p. 151.
[17] Mahesh and Seshadri, *Proc. Indian Acad. Sci.*, 1955, **41**, *A*, 210.
[18] Cahn, Ingold, and Prelog, *Experientia*, 1956, **12**, 81.
[19] Kulkarni and Joshi, *J. Indian Chem. Soc.*, 1957, **34**, 753.
[20] King and Clark-Lewis, *J.*, 1955, 3384.
[21] Keppler, *J.*, 1957, 2721.

	5,7,3′,4′-Me_4 ether of (+)-catechin		5,7,3′,4′-Me_4 ether of (−)-epicatechin		5,7,4′-Me_3 ether of (−)-epiafzelechin		5,7,4′-Me_3 ether of new flavan-3-ol	
	M. p.	$[\alpha]_{Hg}$ [a]	M. p.	$[\alpha]_{Hg}$ [a]	M. p.	$[\alpha]_D$ [b]	M. p.	$[\alpha]_D$ [b]
3-OH	143—144°	−13·4°	153—154°	−61·5°	110°	−67° [e]	135°	−3·4° [e], −3·0°
3-OAc	95—96	+6·8	91—92	−71·2	133	−73·8	92—93	+16
3-OTos	86—88° [c]	+87·7 [d]	~165	−16·9	165	−9	130	+63
	115—116							

The above values, except those for the new flavanol and its derivatives, are from King, Clark-Lewis, and Forbes, *J.*, 1955, 2948.

[a] In $(CHCl_2)_2$. [b] In $CHCl_3$, except as stated in note *e*. [c] Two forms; see Clark-Lewis and Korytnyk, *J.*, 1958, 2367. [d] $[\alpha]_D$. [e] In EtOH.

group normally give a preponderance of the equatorial isomer.[22,23] However, Kulkarni and co-workers [19,24,25] obtained mixtures of *cis*- and *trans*-3,4-diols on reduction of dihydrofisetin and dihydro-4′-methoxy-6-methylflavonol by lithium aluminium hydride, and when the carbonyl group is hindered as in dihydroquercetin tetrabenzyl ether such reduction gives only the *cis*-3,4-diol (3*eq*, 4*ax*).[26] The difference in the course of the catalytic reduction of (+)-dihydrokæmpferol trimethyl ether in ethanol and in acetic acid is not a general one. Bognar and Rakosi [22] found that the reduction of dihydroflavonol by hydrogen over a supported palladium catalyst gives the *trans*-3,4-diol in both solvents. Keppler,[21] however, showed that dihydrofisetin gives the corresponding *cis*-3,4-diol by reduction over a platinum catalyst in methanol, and Kulkarni and co-workers [19,23,24] found that similar reduction of 7,8,3′,4′-tetramethoxydihydroflavonol in acetic acid gives the *cis*-3,4-diol, and not the flavan-3-ol.

Of the successive light petroleum, ether, and acetone extracts of rauli, the petroleum extract yielded intractable fatty material and the ether extract gallic acid and a small quantity of a methanol-soluble glycoside found in greater amount in the acetone extract. Two crystalline glycosides were found in the acetone extract, one being obtained as an insoluble residue (0·4%) on treating the crude extract with methanol, and the other (1·2%) being isolated from the evaporated methanol liquors. Both glycosides on acid-hydrolysis afforded dihydrokæmpferol and L-rhamnose in equimolar amounts, and on methylation followed by hydrolysis both gave dihydrokæmpferol 5,7,4′-trimethyl ether. The two glycosides, which are therefore stereoisomeric dihydrokæmpferol 3-L-rhamnosides, have been isolated previously from the bark of *Engelhardtia formosana* [8,27] and named engelitin and isoengelitin, and a comparison with authentic samples confirmed the identity.

In the present work acid-hydrolysis of engelitin has given a fully active sample of (+)-dihydrokæmpferol, $[\alpha]_D$ +48°; but hydrolysis of isoengelitin is more difficult owing to its low solubility, and partially racemised (−)-dihydrokæmpferol, $[\alpha]_D$ −36°, was obtained. At first this was taken as evidence that engelitin and isoengelitin were (+)- and (−)-dihydrokæmpferol 3-L-rhamnoside respectively. However, recently Tominaga obtained two other stereoisomers, neoengelitin and neoisoengelitin, by isomerisation of engelitin in hot aqueous pyridine and showed that neoengelitin readily gives fully active (−)-dihydrokæmpferol on hydrolysis, which suggests that this isomer is (−)-dihydrokæmpferol 3-L-rhamnoside; [28] further, Tominaga considers isoengelitin to be the *cis*-isomer (−)-epidihydrokæmpferol 3-L-rhamnoside. The isolation of partially racemised (−)-dihydrokæmpferol on hydrolysis of isoengelitin can be accommodated by this structure if it is assumed that the *cis*-form reverts to the more stable *trans*-form by an epimerisation which occurs more rapidly at one centre than the other.

[22] Bognar and Rakosi, *Chem. and Ind.*, 1956, 188; *Acta Chim. Acad. Sci. Hung.*, 1956, **14**, 369.
[23] Kulkarni and Joshi, *Chem. and Ind.*, 1954, 1456.
[24] Kulkarni and Joshi, *Chem. and Ind.*, 1954, 1421.
[25] Chandorkar and Kulkarni, *Current Sci.*, 1957, **26**, 345.
[26] Freudenberg and Weinges, *Annalen*, 1958, **613**, 71.
[27] Tsukamoto and Tominaga, *J. Pharm. Soc. Japan*, 1953, **73**, 1172; *Chem. Abs.*, 1954, **48**, 12740; Tominaga, *ibid.*, 1955, **75**, 1399; *Chem. Abs.*, 1956, **50**, 9396.
[28] Tominaga, personal communication.

Experimental

Ultraviolet absorption spectra refer to ethanol solutions, and were determined on a Unicam S.P. 500 spectrophotometer.

Extraction of Heartwoods.—The comminuted wood (3·0 kg.) was extracted successively with light petroleum (b. p. 40—60°), ether, acetone, and ethanol, for 18 hr. under nitrogen in a continuous-return extractor. In each case, the solvent was removed by evaporation to give the extract.

Coigue Extracts.—The combined yellow, waxy, petroleum and ether extracts (15 g.) were saponified by a boiling 20% solution of potassium hydroxide in ethylene glycol (50 ml.) for 1 hr. The acidic fraction, isolated in the usual way, yielded ferulic acid (1·0 g., 0·03%), m. p. 167—169°. Recrystallisation from water (charcoal) provided a pure sample, m. p. 168—170° (lit.,[29] 168—169°) (Found: C, 62·1; H, 5·1. Calc. for $C_{10}H_{10}O_4$: C, 61·8; H, 5·2%), which did not lower the m. p. of a synthetic sample.[30] Acetylation by acetic anhydride and pyridine at 100° gave ferulic acid acetate, m. p. 197° (lit.,[31] 196—197°).

The acetone extract, an orange gum (62 g.), was boiled with water (*ca.* 2 l.), leaving an undissolved solid, which after having been washed with methanol, gave crude ellagic acid (8·9 g., 0·3%), which did not melt below 360° and was characterised by its blue ferric reaction, positive Greissmeyer reaction, and the preparation of a tetraethoxycarbonyl derivative [32] by boiling sodium ellagate (0·3 g.) with ethyl chloroformate (10 ml.) for 3 hr. The chloroformate solution was hydrolysed by stirring it with water and gave a solid, which was purified by recrystallisation from acetone to give the derivative, m. p. 249° (lit.,[32] 247°) (Found: C, 52·9; H, 4·1. Calc. for $C_{26}H_{22}O_{16}$: C, 52·9; H, 3·8%).

Extraction of the water-soluble portion of the acetone extract with ethyl acetate, followed by evaporation, gave a residue, which was crystallised from water to yield crude (+)-dihydrokæmpferol (32 g., 1·1%), m. p. 233°. Several recrystallisations from water (charcoal) gave a pure sample, which crystallised in needles, m. p. 241—242° (Pyrex tube); lit.,[4] 237—241°, $[\alpha]_D^{18}$ +56° (*c* 2·0 in 1 : 1 acetone–water) (Found: C, 56·7; H, 5·2. Calc. for $C_{15}H_{12}O_6,1{\cdot}5H_2O$: C, 57·1; H, 4·8. Found, in a specimen dried at 120° *in vacuo*: C, 62·6; H, 4·6; loss, 9·3. Calc. for $C_{15}H_{12}O_6$: C, 62·5; H, 4·2; loss, 8·9%), $\lambda_{max.}$ 290 mμ (log ε 4·16), $\lambda_{min.}$ 248 mμ (log ε 3·32), infl. *ca.* 330 mμ. The dihydroflavonol had a violet-brown ferric reaction, and gave a rose-red colour in the sodium amalgam–ethanol, magnesium–hydrochloric acid, and zinc–hydrochloric acid tests. A solution in hot 4% aqueous sulphuric acid was oxidised by a current of air to kæmpferol.[1]

(+)-Dihydrokæmpferol 3,7,4′-triacetate, prepared by Brewerton's method,[7] had m. p. 135° (lit., 135°), $[\alpha]_D^{18}$ +49° (*c* 1·5 in $CHCl_3$); the racemic triacetate had m. p. 171—172°.

Methyl Ethers of Dihydrokæmpferol.—With excess of diazomethane, dihydrokæmpferol afforded a 7,4′-dimethyl ether, m. p. 196° (Pyrex), 187° (soda glass) (lit.,[4] 187°); (+)-dihydrokæmpferol 5,7,4′-trimethyl ether, m. p. 149° (lit.,[33] 142°), $[\alpha]_D^{18}$ −15·2° (*c* 2·4 in $CHCl_3$), +9·6° (*c* 0·5 in EtOH), was obtained by the action of dimethyl sulphate and potassium carbonate in acetone. The trimethyl ether forms a 3-*acetate*, m. p. 126—128°, $[\alpha]_D^{19}$ +24° (*c* 2·0 in $CHCl_3$) (Found: C, 64·3; H, 5·5. $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%).

When (+)-dihydrokæmpferol trimethyl ether was dissolved in 5% ethanolic potassium hydroxide at room temperature and kept for 3 min. it was converted in 85% yield into kæmpferol 5,7,4′-trimethyl ether, m. p. 149—151° (lit.,[5] 151°) depressed to 130° by the starting compound; this product had $\lambda_{max.}$ 257, 308, 352 mμ (log ε 4·00, 3·72, 4·04).

(+)-5,7,4′-*Trimethoxyflavan*-3-*ol.*—(+)-Dihydrokæmpferol trimethyl ether (0·96 g.) in acetic acid (30 ml.) over reduced platinum oxide (0·25 g. of oxide) absorbed 220 c.c. (N.T.P.) of hydrogen (3 mols.) in 220 min. Removal of the acetic acid from the filtered solution under reduced pressure gave a syrup which crystallised under methanol (yield, 0·45 g., 47%) and recrystallised from ether–light petroleum as needles of 5,7,4′-*trimethoxyflavan*-3-*ol*, m. p. 135°, $[\alpha]_D^{19}$ −3·4° (*c* 0·6 in EtOH), −3·0° (*c* 1·7 in $CHCl_3$) (Found: C, 68·1; H, 6·7. $C_{18}H_{20}O_5$ requires C, 68·3; H, 6·4%), $\lambda_{max.}$ 207, 272 mμ (log ε 4·54, 3·37), $\lambda_{min.}$ 251 mμ (log ε 3·07), infl. 223 mμ.

5,7,4′-*Trimethoxyflavan*-3-*yl acetate*, obtained by use of boiling acetic anhydride and pyridine

[29] Tiemann, *Ber.*, 1896, **9**, 416.
[30] Johnson in " Organic Reactions," Wiley and Sons, New York, 1942, Vol. I, p. 250.
[31] Tiemann and Nagai, *Ber.*, 1878, **11**, 647.
[32] Reichel and Schwab, *Annalen*, 1942, **550**, 152.
[33] Goel, Narasimhachari, and Seshadri, *Proc. Indian Acad. Sci.*, 1954, **39**, *A*, 254.

(1 hr.), formed needles, m. p. 92—93°, $[\alpha]_D^{19}$ +16° (*c* 1·0 in $CHCl_3$) (Found: C, 67·0; H, 6·1; $C_{20}H_{22}O_6$ requires C, 67·0; H, 6·2%).

In pyridine at 100° the flavan-3-ol gave *5,7,4′-trimethoxyflavan-3-yl toluene-p-sulphonate* which crystallised first from ethanol and then from light petroleum (b. p. 80—100°) as needles, m. p. 130°, $[\alpha]_D^{19}$ +63° (*c* 1·1 in $CHCl_3$) (Found: C, 63·8; H, 5·7. $C_{25}H_{26}O_7S$ requires C, 63·8; H, 5·6%).

5,7,4′-Trimethoxyflavan-3,4-diol.—A solution of (+)-dihydrokæmpferol trimethyl ether (1·00 g.) in ethanol (45 ml.) over reduced platinum oxide (0·1 g. of oxide) absorbed 74·5 c.c. (N.T.P.) of hydrogen (1·04 mols.) in 30 min. The filtered solution was evaporated to a residue, which after several recrystallisations from ethanol–light petroleum (b. p. 80—100°) gave needles of *5,7,4′-trimethoxyflavan-3,4-diol*, m. p. 161—162°, $[\alpha]_D^{19}$ +3·6° (*c* 1·2 in $CHCl_3$), +8·0° (*c* 0·6 in EtOH) (Found: C, 65·2; H, 6·3. $C_{18}H_{20}O_6$ requires C, 65·0; H, 6·1%).

A slurry of (+)-dihydrokæmpferol trimethyl ether (0·5 g.) in methanol (30 ml.) was added in portions to a solution of sodium borohydride (0·2 g.) in methanol (5 ml.); the solid gradually dissolved. After 45 min. the solution was poured into N-sodium hydroxide (100 ml.), and the whole was extracted with ether. The extracted solid (0·40 g., 80%) was repeatedly recrystallised from ethanol–light petroleum (b. p. 80—100°), to give needles, m. p. 161—162°, undepressed on admixture with the hydrogenation product.

Finely ground (+)-dihydrokæmpferol trimethyl ether (1·0 g.) and ether (50 ml.) were added as a slurry to a boiling ethereal solution (20 ml., 4·5%) of lithium aluminium hydride. Boiling was continued for 7 hr., and the solution was kept overnight at room temperature. Excess of hydride was decomposed by methanol, then the mixture was shaken with N-sodium hydroxide (100 ml.), and the product collected in ether. The crude diol (0·98 g., 97%) obtained, when purified, was identical with the above diol.

On heating with concentrated hydrochloric acid, a solution of the diol gave a red colour which was extracted by pentyl alcohol.

The 3,4-diol (0·3 g.), when boiled with acetic anhydride (3 ml.) and pyridine (3 ml.) for 20 min., gave *3,4-diacetoxy-5,7,4′-trimethoxyflavan*, plates, m. p. 144—145° (from ethanol), $[\alpha]_D^{19}$ + 1·6° (*c* 1·4 in $CHCl_3$) (Found: C, 63·2; H, 5·8. $C_{22}H_{24}O_8$ requires C, 63·4; H, 5·8%).

Configuration of the 3,4-Diol.—Triethylamine (2 ml.) was added dropwise to a solution of the 3,4-diol (0·2 g.) in benzene (2 ml.), dioxan (2 ml.), and ethyl chloroformate (2 ml.), the mixture was kept at room temperature for 2 hr., then filtered, and the filtrate allowed to evaporate. The portion of the residue soluble in hot light petroleum (b. p. 80—100°) recrystallised from methanol as needles (0·08 g.), m. p. and mixed m. p. with the starting compound 160°.

A solution of the diol (0·1 g.) in acetone (6 ml.) containing concentrated hydrochloric acid (1 drop in 100 ml.) was kept at room temperature for 3 days, then treated with triethylamine (2 drops). Addition of water to the solution gave a product which did not crystallise.

The pH of a solution (50 ml.) of mannitol (0·1 g.) in 50% aqueous ethanol was adjusted to 10·6 with sodium carbonate solution. A solution (pH 10·8) of sodium borate (0·27 g.) in 50% aqueous ethanol (100 ml.) was then added in portions. On addition of 1·2 ml., the pH fell to 6·5. When the 3,4-diol was used in the above procedure, the change in pH was less than 0·2.

Rauli Extracts.—The ether extract, a red gum (6·1 g.), was leached with hot chloroform, leaving an insoluble fraction (2·7 g.) which was crystallised from water, yielding crude engelitin, m. p. 160—170° (1·0 g., 0·03%). Concentration of the mother-liquor gave gallic acid, m. p. 220—235° (decomp.) (0·7 g., 0·02%), which recrystallised from water as needles, m. p. 239—244° (decomp.) [lit.,[34] 239—240° (decomp.)] (Found: C, 49·4; H, 3·6. Calc. for $C_7H_6O_5$: C, 49·1; H, 3·5%). Treatment with ethereal diazomethane gave methyl tri-*O*-methylgallate, m. p. and mixed m. p. 81·5°.

The acetone extract, a dark red gum (123 g.), was treated with cold methanol (*ca.* 500 ml.), leaving undissolved crude isoengelitin, m. p. 285° (decomp.) (12·0 g., 0·4%). The dark red methanol solution was evaporated to dryness and the residue was boiled with water (2 l.). The filtered aqueous solution was extracted several times with ethyl acetate, and the combined extracts were evaporated to a solid, which when crystallised from water gave crude engelitin, m. p. 160—170° (36·1 g., 1·2%).

Engelitin and Isoengelitin.—Crude engelitin was purified by recrystallisation from water to give plates, m. p. 172°, $[\alpha]_D^{19}$ −18·3° (*c* 1·4 in C_5H_5N) (lit.,[35] m. p. 176—177°, $[\alpha]_D$ −16°)

[34] Perkin and Hummel, *J.*, 1896, **69**, 1292.
[35] Tominaga and Joshimura, *J. Pharm. Soc. Japan*, 1959, **79**, 555.

(Found: C, 54·7; H, 5·5. Calc. for $C_{21}H_{22}O_{10},1{\cdot}5H_2O$: C, 54·7; H, 5·5. Found, in a sample dried at 140° *in vacuo*: C, 57·8; H, 5·3. Calc. for $C_{21}H_{22}O_{10}$: C, 57·8; H, 5·1%), $\lambda_{max.}$ 291 mμ (log ε 4·15), $\lambda_{min.}$ 251 mμ (log ε 3·37), infl. *ca.* 325 mμ.

Isoengelitin was purified by concentrating a solution in 50% aqueous acetone until a precipitate was formed; it then crystallised in blades, m. p. 292° (decomp.), $[\alpha]_D^{22}$ −280° (*c* 0·5 in C_5H_5N) [lit.,[35] m. p. 301—302° (decomp.), $[\alpha]_D^{18}$ −282°] (Found: C, 57·9; H, 5·1%), $\lambda_{max.}$ 290 mμ (log ε 4·17), $\lambda_{min.}$ 248 mμ (log ε 3·38), infl. *ca.* 335 mμ.

Both engelitin and isoengelitin give violet–brown ferric reactions and positive sodium amalgam–ethanol and magnesium–hydrochloric acid tests. The infrared spectra (Nujol mulls) of engelitin and isoengelitin were identical with those of authentic samples kindly supplied by Dr. T. Tominaga.

Hydrolysis of Engelitin.—The glycoside (1·0007 g.) was added to hot 6% aqueous sulphuric acid (25 ml.), and the solution was boiled for 20 min., then kept overnight at 0°. The colourless crystals formed were collected and the filtrate and washings were retained.

The dried aglycone (0·6950 g., 92% calc. on the basis of one rhamnose unit per molecule) separated from water as needles, m. p. 241—242° (Pyrex), $[\alpha]_D^{19}$ +48° (*c* 2·4 in 1 : 1 acetone–water). When acetylated as described for dihydrokæmpferol, the compound formed (+)-dihydrokæmpferol triacetate, m. p. and mixed m. p. 135°, $[\alpha]_D^{19}$ +54° (*c* 1·8 in $CHCl_3$).

The solution and washings from which the aglycone had been removed were heated on a steam-bath and neutralised with barium carbonate. After removal of the precipitated sulphate, the filtrate was concentrated to 10 ml. A portion (4 ml.) of this solution, treated with phenylhydrazine acetate under standard conditions,[36] precipitated an osazone in 9 min. Its crystalline form was identical with that of a specimen similarly prepared from L-rhamnose, and after recrystallisation from ethanol it had m. p. and mixed m. p. 181°, $[\alpha]_D^{20}$ +92° (*c* 0·4 in C_5H_5N) (lit.,[37] +94°).

Hydrolysis of Isoengelitin.—The glycoside (0·1655 g.) dissolved in 6% aqueous sulphuric acid (25 ml.) only after being boiled for 4 hr. Treatment of the hydrolysis mixture in the same way as that from engelitin gave the aglycone (0·0982 g., 90% based on one rhamnose unit per molecule), $[\alpha]_D^{20}$ −21° (*c* 1·3 in 1 : 1 acetone–water), and, from the filtrate, L-rhamnosazone, m. p. and mixed m. p. 181°, $[\alpha]_D^{20}$ +93° (*c* 0·5 in C_5H_5N), was obtained 9 min. after the addition of phenylhydrazine acetate.

The glycoside (0·3 g.), when added to boiling 5% sulphuric acid (300 ml.), dissolved completely in 40 min. After cooling, the solution was extracted with ether, and the extract was evaporated to a residue which recrystallised from water as needles, m. p. 240—241° (Pyrex), $[\alpha]_D^{19}$ −36° (*c* 1·2 in 1 : 1 acetone–water). Acetylation of this product gave partially racemic dihydrokæmpferol triacetate, m. p. 155—162°, $[\alpha]_D^{17}$ −30° (*c* 1·5 in $CHCl_3$), whose infrared spectrum in chloroform was identical with that of (+)-dihydrokæmpferol triacetate.

Methylation of Engelitin and Isoengelitin.—Engelitin (0·5 g.) was dissolved in dry acetone (50 ml.), and dimethyl sulphate (0·5 ml.) and potassium carbonate (2·5 g.) were added. The stirred mixture was boiled under reflux for 2 hr. and the solution was then filtered and evaporated to dryness under reduced pressure. A solution of the pale yellow residue in 3% methanolic hydrogen chloride (30 ml.) was boiled for 1 hr. It was then diluted with water (150 ml.) and extracted with ether; the ether extract yielded a residue which recrystallised from methanol as prisms (0·14 g., 40%), m. p. 149°, undepressed when mixed with dihydrokæmpferol 5,7,4′-trimethyl ether.

By the same procedure isoengelitin (0·5 g.) gave the same product (0·15 g., 40%), m. p. and mixed m. p. 150°.

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[36] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 442.
[37] Fischer and Zach, *Ber.*, 1912, **45**, 3771.