513. *The Structure of Flindissol. Some Remarks on the Elemi Acids.*

By A. J. BIRCH, D. J. COLLINS, SULTAN MUHAMMAD, and J. P. TURNBULL.

Flindissol is shown to have the structure (Ia) by its reactions and by identity of a derivative with (VIb) obtained from elemadienolic acid (" α-elemolic " acid). The structure of the latter is amended to (XVb), containing a 7-double bond; " β-elemonic acid " (XVI) has an 8(9)-double bond.

FLINDISSOL was isolated from the bark and leaves of *Flindersia dissosperma* Domin. and from the bark of *Flindersia maculosa* Lindl.[1] The formula, $C_{30}H_{48}O_3$, is supported by ebullioscopic and *X*-ray examination of flindissone lactone. For simplification of exposition the evidence for its structure will be discussed in terms of the formula (Ia), ultimately shown to represent it.

Nucleus.—Dehydrogenation of flindissol by selenium at 320° gives 1,2,8-trimethylphenanthrene in 1·1% yield, identified by spectra and by comparison with an authentic specimen kindly provided by Dr. T. G. Halsall. This hydrocarbon has been obtained from all the usual types of tetracyclic triterpene, *e.g.*, lanosterol,[2] euphol,[3] polyporenic acid-A,[4] and elemadienolic acid.[5] That the nucleus is probably that of euphol or tirucallol was first indicated by oxidation of deoxydihydroflindissyl acetate (IIf) by perbenzoic acid to a product which is not crystalline but has the ultraviolet absorption characteristic [6] of a 7,9(11)-diene in this stereochemical series ($\lambda_{max.}$ 231·5, 238·5, and 247 mμ).

Substituents.—Flindissol (Ia) contains a 3α(*ax*)-hydroxyl group and a cyclic semiacetal group with a five-membered ether ring. Mild oxidation with chromium trioxide in pyridine gives flindissone lactone (Ib), $C_{30}H_{44}O_3$, $\nu_{max.}$ 1775 (lactone) and 1710 cm.$^{-1}$ (six-ring ketone). The lactone ring is very resistant to hydrolysis, but in one experiment a hydroxy-acid, $C_{30}H_{46}O_4$, was obtained. In some oxidations a minor product was flindissone (Ic), $C_{30}H_{46}O_3$, $\nu_{max.}$ 3430 (OH) and 1710 cm.$^{-1}$ (six-ring ketone), and this can be further oxidised to flindissone lactone (Ib).

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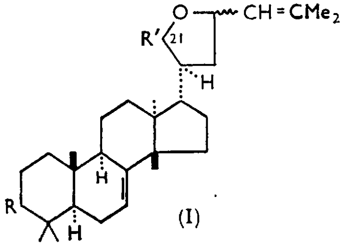
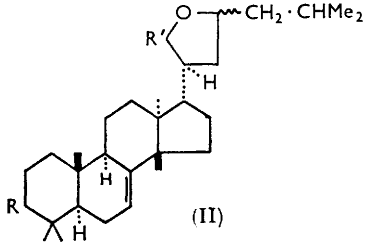
[1] Brown, Gilham, Hughes, and Ritchie, *Austral. J. Chem.*, 1954, **7**, 181.
[2] Ruzicka, Rey, and Muhr, *Helv. Chim. Acta*, 1944, **27**, 472.
[3] Barton, McGhie, Pradhan, and Knight, *J.*, 1955, 876.
[4] Halsall, Jones, and Lemin, *J.*, 1953, 468.
[5] Ruzicka, Rey, and Spillmann, *Helv. Chim. Acta*, 1942, **25**, 1375.
[6] Halsall, Meakins, and Swayne, *J.*, 1953, 4139.

The rather unusual α-orientation of the 3-hydroxyl group, also found in elemadienolic acid[5] and polyporenic acid-A,[4] is indicated by a number of reactions. Reduction of flindissol with lithium aluminium hydride or sodium borohydride removed directly the acetal-hydroxyl group to give deoxyflindissol (Id), $C_{30}H_{48}O_2$, which yields a monoacetate and on oxidation gives the ketone deoxyflindissone (Ie), $C_{30}H_{46}O_2$, $\nu_{max.}$ 1708 cm.$^{-1}$. Reduction of deoxyflindissone with sodium and propan-2-ol or sodium borohydride produces 3-epideoxyflindissol (If), $C_{30}H_{48}O_2$. Since the reduction processes should give a 3β-hydroxyl group,[7] flindissol must contain a 3α-hydroxyl group. The molecular-rotation difference on acetylation of deoxyflindissol, ΔM_D −144°, is of the order to be expected for an axial alcohol.[8]



(I)

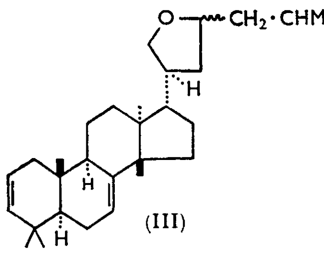
	R	R′
a	H, α-OH	H, α-OH
b	=O	=O
c	=O	H, α-OH
d	H, α-OH	H_2
e	=O	H_2
f	H, β-OH	H_2
g	H, α-OAc	H, α-OAc
h	H, α-OAc	=O



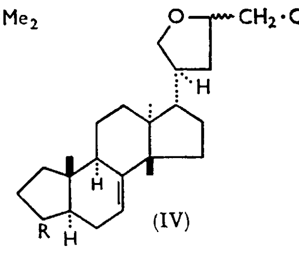
(II)

	R	R′
a	H, α-OH	H, α-OH
b	=O	=O
c	H, α-OH	H_2
d	H, β-OH	H_2
e	=O	H_2
f	H, α-OAc	H_2

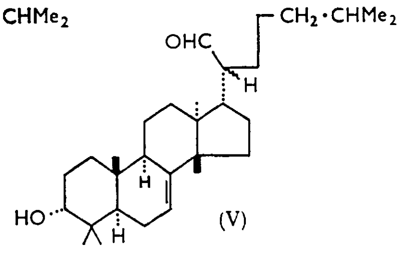
This orientation and location at the 3-position is supported by dehydrations. The side-chain double bond of deoxyflindissol is readily hydrogenated without the nuclear double bond's being affected (see below), and the resulting deoxydihydroflindissol (IIc) is smoothly dehydrated by phosphorus pentachloride to 21(23)-epoxytirucalla-2,7-diene (III), which is hydroxylated by osmium tetroxide to give the crystalline 2,3-diol. This diol is cleaved by lead tetra-acetate without formation of a volatile ketone; an axial 3α-alcohol would be expected to be dehydrated without rearrangement, affording a 2,3-double bond.[7] The equatorial epimer (IId), obtained as above by borohydride reduction of deoxydihydroflindissone (IIe), undergoes the rearrangement characteristic[7] of other triterpenoid 3β-alcohols on dehydration with phosphorus pentachloride. The product did not crystallise, but hydroxylation and cleavage of the derived diol as above give acetone and formaldehyde in the ratio of about 4 : 1. The non-volatile portion, which did not



(III)



(IV)



(V)

(a: R = :CMe_2) (b: R = H, CMe:CH_2)

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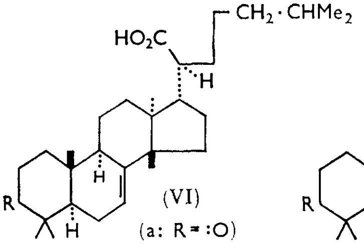
[7] Barton, *J.*, 1953, 1027.

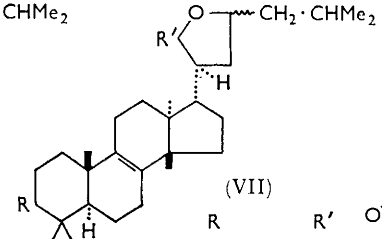
[8] Klyne and Stokes, *J.*, 1954, 1979.

crystallise, has absorption bands at 1738s (five-ring ketone) and 1704m cm.$^{-1}$ (methyl ketone ?). These results can be explained by the dehydration: (IId) ⟶ (IVa) + (IVb).

A remarkable dimerisation of flindissol is clearly pertinent to the stereochemistry of the side-chain hydroxyl group. A dianhydro-dimer, $C_{60}H_{92}O_4$, is produced by a variety of reactions including heating flindissol to about 230° or, better, by warming it in glacial acetic acid. Its formula is supported by Rast molecular-weight determinations and by *X*-ray crystallography. The spectrum has a series of bands (1090, 1060, 1030, 1010, and 980 cm.$^{-1}$) indicative of an acetal group,[9] but none due to a hydroxyl or carbonyl group. Ether formation under such mild conditions was the first indication of the presence of a semiacetal group. The compound must be produced by reaction of the 3α-hydroxyl group of one molecule with the semiacetal group of the other, forming a macrocycle; the steric implications are discussed below.

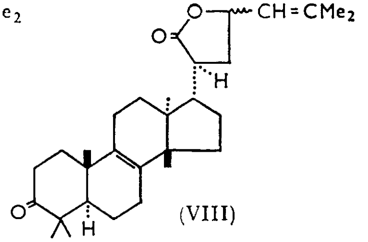


(VI)
(a: R = :O)
(b: R = H, α-OAc)



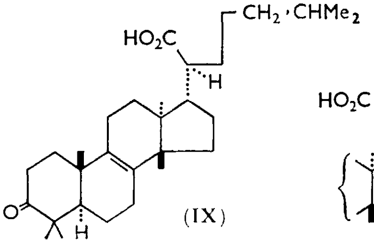
(VII)

	R	R′
a	H,α-OH	H_2
b	H,α-OH	=O
c	=O	=O
d	H,β-OH	=O
e	=O	H_2

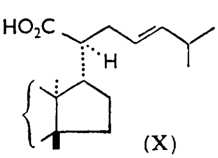


(VIII)

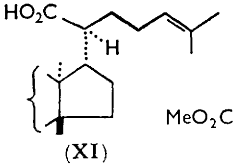
Acetylation of flindissol gives a mixed product. A crystalline compound, $(C_{32}H_{50}O_4)_n$, could be the 3α-monoacetyl derivative of flindissol or, more probably, the diacetyl derivative of an anhydro-dimer produced by linkage of two molecules through the semiacetal groups. The remaining uncrystallisable gum is probably chiefly diacetylflindissol (Ig); it was oxidised with chromic acid in the expectation that the semiacetal ester would be unstable and preferentially oxidised to a lactone. The product is in fact acetylflindissol lactone (Ih), and on hydrogenation gives an acid shown ultimately to be acetyldihydro-" α-elemolic " acid (VIb) (see below).



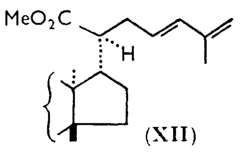
(IX)



(X)



(XI)



(XII)

Double Bonds.—One double bond must be in a C=CMe$_2$ group since ozonolysis of flindissone lactone (Ib) gives acetone in good yield. The relation of this double bond to the semiacetal group is demonstrated by hydrogenolysis and by acid treatment of several derivatives.

Hydrogenation of flindissol (Ia) with palladium–carbon in methanol containing 0·1N-hydrochloric acid gives, by fission of an ether bond, a mixture of aldehydes (V), $C_{30}H_{50}O_2$,

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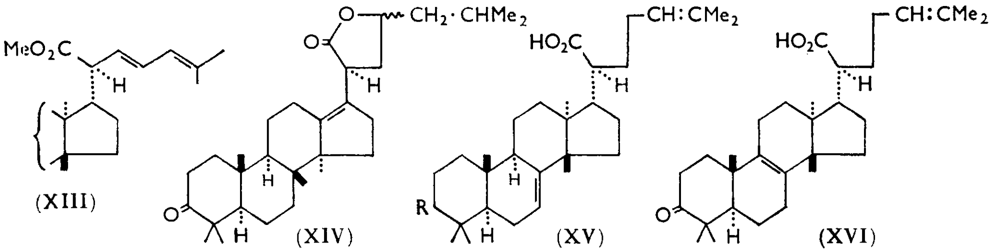
[9] West, " Chemical Applications of Spectroscopy," Interscience Publishers, New York, 1956, p. 442.

one of which is crystalline, with $\nu_{max.}$ 3630 (OH), 2720, and 1708 cm.$^{-1}$ (aldehyde), thus indicating an allyl ether group in flindissol. A similar reaction of acetylflindissol lactone (Ih) gives acetyldihydro-" α-elemolic " acid (acetylisoelemenolic acid, 3α-acetoxytirucall-7-en-21-oic acid) (VIb), identical with an authentic specimen. Hydrogenation in presence



(XIII) (XIV) (XV) (XVI)

of acidic palladium–carbon [10a] in ethyl acetate or Adams catalyst in acetic acid produces about 50% of hydrogenolysis and 50% of hydrogenation: flindissone lactone (Ib) thus gives dihydro-" α-elemonic " acid (VIa) and, if palladium is used, dihydroflindissone lactone (IIb), or, if platinum is used, dihydroisoflindissol lactone (VIIb); isoflindissone lactone (VIII) gave dihydro-" β-elemonic " acid (IX) and, if palladium is used, dihydroisoflindissone lactone (VIIc). Using alkaline palladium–carbon [10b] in the hydrogenation gave only dihydroflindissol (IIa) from flindissone, and dihydroflindissol lactone (IIb) from flindissone lactone. These dihydro-compounds no longer contain the isopropylidene group since they no longer give acetone on ozonolysis. Retention of the original double-bond position in the acid (VIa), but not in the lactone (VIb), during Adams hydrogenation of flindissone lactone is probably due to the insolubility of the acid, which causes it to be precipitated during the reaction. Other examples of shift of a 7-double bond to the 8(9)-position under similar hydrogenation conditions are known.[11] Dihydroisoflindissone lactone (VIIc) is not converted into an acid by hydrogenation with Adams catalyst, but only into dihydroisoflindissol lactone (VIIb) (above), thus demonstrating the necessity of the side-chain double bond for hydrogenolysis. It is notable that the hydrogenation of the 3-carbonyl group with Adams catalyst to produce the alcohol (VIIb) is the only process so far observed which generates the natural 3α-configuration.

That hydrogenolysis is not dependent on a preliminary shift of the double bond is shown by direct reduction of flindissone lactone with lithium in liquid ammonia. The acid (partial structure X) is the main product, but some of the isomer (partial structure XI) is also formed. The mixture is irresolvable but on oxidation by chromic acid and catalytic hydrogenation of the products gives the keto-acid (VIa) that was obtained previously by hydrogenolysis. Ozonolysis of the mixture (X—XI) gives isobutyraldehyde and acetone in the ratio 5 : 1, showing the proportions of the components in the mixture. This result confirms the view that the double bond concerned in the hydrogenolysis is that initially in the C=CMe$_2$ group. Such hydrogenolyses proceed through mesomeric anions [12] and it is unexpected that protonation should occur at the more highly substituted end. The result is presumably due to the bulky ring system adjacent to the less substituted end, thus decreasing solvation and increasing steric hindrance there.

Final confirmation of the relative position of the lactone and the isopropylidene groups comes from an examination of the action of methanolic hydrochloric acid on flindissone lactone (Ib). With increasing severity of conditions, two isomeric methyl esters are obtained in succession: mild reaction (warming to 40°) gives a compound $C_{31}H_{46}O_3$, whose infrared absorption is in accord with the conjugated-diene side-chain as in (XII);

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[10] Vogel, " Practical Organic Chemistry," Longmans, Green and Co., 1954, pp. (*a*) 996, (*b*) 824.
[11] Dawson, Halsall, Jones, Meakins, and Philips, *J.*, 1956, 3172.
[12] Birch, *J.*, 1945, 809.

the mixture gives an isomeric ester, whose absorption indicates structure (XIII). No diene is produced from dihydroflindissone lactone (IIb) on similar treatment, which gives only dihydroisoflindissone lactone (VIIc).

The second double bond migrates from a trisubstituted ($\nu_{max.}$ 830 cm.$^{-1}$) to a tetrasubstituted position, not only under the action of Adams catalyst, but also under that of hydrogen chloride in chloroform or boiling methanol. The shift during Adams hydrogenation of flindissone lactone has already been noted. A second example occurs when deoxydihydroflindissol (IIc) is shaken with Adams catalyst in glacial acetic acid. No hydrogen is absorbed and the product is deoxydihydroisoflindissol (VIIa), which is oxidised by chromic acid to deoxydihydroisoflindissone (VIIe). Deoxydihydroisoflindissol (VIIa) is also the major product of hydrogenation of flindissol (Ia) in presence of Adams catalyst in glacial acetic acid.

The nuclear magnetic resonance spectrum of flindissone lactone (Ib) shows two ethylenic protons in the region τ 4·8 as a complex series of bands. Only one of these is on the side-chain double bond: the other must be on the nuclear double bond. That the double bond migrates from the 7- to the 8(9)-position is shown by examination of the optical rotatory dispersion curves of flindissone lactone (Ib) and of isoflindissone lactone (VIII) (obtained from the former by the action of hydrogen chloride in dry chloroform at 0°). These curves are practically superimposable on those of masticadienonic and isomasticadienonic acid[13] which are known to contain a 7- and a 8(9)-double bond, respectively.[14]

More drastic acid treatment in the euphol series results in methyl as well as proton migrations, to give isoeuphol derivatives.[3] When dihydroisoflindissone lactone (VIIc) is heated with acetic acid containing 2N-aqueous sulphuric acid,[3] it produces an isomer (XIV), whose optical rotation (+14°) is close to that expected.

Stereochemistry of the Side-chain.—The carbon skeleton is completely defined by the relationship to " α-elemolic " acid and therefore to tirucallol. It is not possible at present to define the stereochemistry of the centre carrying the isobutenyl group. Examination of models shows that the dianhydro-dimer can be formed readily only if the 21-hydroxyl group is α-oriented as in (Ia). However, this assignment is only tentative since the dimerisation might involve inversion at this centre.

Relation to the Elemi Acids.—Indications of a euphane–tirucallane skeleton (see above) came late in the experimental sequence and led to a search for a known substance for comparison. The most obvious series appeared to be that of the elemi acids, which were thought to contain an 8(9)-double bond in a tirucallane skeleton[15] and might presumably be related to the isoflindissol series. In fact, however, hydrogenolysis of the lactone (Ih) without migration of the 7-double bond (see below) gives acetyldihydro-" α-elemolic " acid (VIb), identical in mixed m. p. and infrared spectrum with a sample prepared by hydrogenation with alkaline palladium–carbon[10b] of authentic acetyl-" α-elemolic " acid (XVc) kindly supplied by Dr. T. G. Halsall.

Since, according to published conclusions (*e.g.*, ref. 15), elemenolic acid should have an 8(9)-double bond we were led to examine critically the literature on the elemi acids, which is in a somewhat confused state, made worse by several changes in nomenclature.

Early work on the elemi acids[16] suggested that two principal acids occur: " α-elemolic " acid, m. p. 224—225°, $[\alpha]_D$ −28°, and " β-elemonic " acid, m. p. 226°, $[\alpha]_D$ +48°, which differ, not only in the oxygen group, but also in the position of the nuclear double bond. This view is summarised:[17] " The non-identity of the dihydro-α- and dihydro-β-elemanic acids coupled with the identity of the triketo-acid derived from both series (*i.e.*, by chromic

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[13] Djerassi, Halpern, Halpern, and Riniker, *J. Amer. Chem. Soc.*, 1958, **80**, 4001.

[14] Barton and Seoane, *J.*, 1956, 4150; Seoane, *J.*, 1956, 4158.

[15] Menard, Syler, Hiestand, Arigoni, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1955, **38**, 1517.

[16] Summarised by Simonsen and Ross, " The Terpenes," Cambridge University Press, 1957, Vol. V, pp. 325—354.

[17] Ref. 16, p. 336.

acid oxidation to the 8(9)-en-3,7,11-trione) suggested that the two series differed in the position of the less reactive (*i.e.*, nuclear) double bond which could, however, migrate to the same position during the formation of the O=C–C=C–C=O chromophore." Doubt was thrown on this view by later detection of varying amounts of the 7,9(11)-diene by ultraviolet spectroscopy. At first, this ultraviolet absorption was thought to represent a pure diene produced by acid isomerisation of one or both of the double bonds into conjugation,[18,19] leading to the introduction of the term " iso " into the literature to remove the " misleading α- and β-prefixes." [19] Later, the nature of the dienic absorption was correctly interpreted as due to the 7,9(11)-dienes.[6] These have high negative optical rotations ($[\alpha]_D \sim -150°$), and the admixture of them, in varying proportions, with the dextrorotatory compounds containing an 8(9)-double bond was thought to explain the negative rotations observed in the old " α " or " iso " series. The proportion of 7,9(11)-diene, measurable by ultraviolet absorption, is, however, too small to provide the sole explanation of the rotations. Halsall and his co-workers [6] considered that " elemenolic " acid had an 8(9)-double bond but expressed the view that " elemadienonic " acid (" α-elemonic " acid) contained, as well as the 8(9)-enoic and the 7,9(11)-dienoic acids, a third, optically transparent compound of high negative optical rotation. This third compound is evidently the 7-enoic acid (XVa) and was almost certainly isolated about 85% pure in one of their reactions. Another misleading factor in the situation, so far as the position of the double bond was concerned, was the reported Meerwein–Ponndorf reduction [19] of " methyl β-elemonate " to a mixture containing mostly " methyl α-elemolate " and only a small amount of " methyl β-elemolate." This result, incomprehensible on present conclusions, unless the starting material was impure, probably led to the use of " methyl dihydro-β-elemonate " as starting material in the conversion of " elemedienolic acid " into tirucallenol and euphenol.[15] The last two compounds were known to contain an 8(9)-double bond,[20] so that it appeared to be proved that " α-elemolic acid " also had an 8(9)-double bond.

Consideration of data in the literature (mainly summarised by Simonsen and Ross [16]) including optical-rotation differences between the epimeric 3-hydroxy- and 3-acetoxy- and the 3-oxo-compounds in the elemi acid and related series,[21] and also comparison of elemi acid derivatives and flindissol derivatives, led us to believe that the view expressed by Simonsen and Ross [17] is correct and that the original " α " series contains a 7- and the " β " an 8(9)-double bond. In order to examine this conclusion further, we have, with the generous assistance of Professor W. Klyne, examined the optical rotatory dispersion curves of authentic elemi acid samples kindly provided by Dr. T. G. Halsall and compared them with similar compounds from the flindissol series. Some small quantitative deviations are probably explained by the presence of variable small amounts of the 7,9(11)-diene but the overall picture confirms the view above. Dihydro-" β-elemonic " acid has the expected positive Cotton effect ($[\phi]_{310}$ +2150°, $[\phi]_{280}$ −1150°) and is comparable with the same substance, 3-oxotirucall-8(9)-en-21-oic acid (IX), from isoflindissone lactone (VIII) ($[\phi]_{310}$ +1950°, $[\phi]_{280}$ −900°). Dihydro-" α-elemonic " acid (VIa) ($[\phi]_{325}$ −2000°, $[\phi]_{290}$ −995°; methyl ester, $[\phi]_{325}$ −1800°, $[\phi]_{290}$ −900°) and " α-elemonic " acid (elemadienonic acid, 3-oxotirucalla-7,24-dien-21-oic acid) (XVa) ($[\phi]_{312}$ −2120°, $[\phi]_{290}$ −470°) have the expected negative Cotton effect curves. Flindissone lactone ($[\phi]_{315}$ −2650°, $[\phi]$ +140°) and isoflindissone lactone ($[\phi]_{305}$ +1140°, $[\phi]_{275}$ −270°) are comparable with masticadienonic acid ($[\phi]_{315}$ −2600°, $[\phi]_{275}$ +100°) and isomasticadienonic acid ($[\phi]_{305}$ +1290°, $[\phi]_{275}$ −1150°). There seems no doubt, therefore, that " β-elemonic acid is 3-oxotirucalla-8(9),24-dien-21-oic acid (XVI) and " α-elemolic " acid is 3α-hydroxytirucalla-7,24-dien-21-oic acid (XVb).

Conversions of the 7- into the 8(9)-double-bond isomers occur readily under the action

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[18] Bilham and Kon, *J.*, 1942, 544.

[19] Ruzicka, Rey, Spillmann, and Baumgartner, *Helv. Chim. Acta*, 1943, **26**, 1638.

[20] See, *e.g.*, Barbour, Bennet, and Warren, *J.*, 1951, 2540.

[21] Collected from Ourisson and Crabbe, " Les Triterpenes Tetracycliques," Hermann, Paris, 1961.

of acid or, in many cases, of Adams catalyst. It appears that any structural conclusions must be treated with caution in this series if either of these reagents is involved and that the discrepancies in the literature are possibly due to unrecognised migrations of this type.

The structural conclusions relate closely the biogenesis of the masticadienonic and of elemadienolic acid series. The two series are probably derived from the same 7-unsaturated isomer of tirucallol by oxidation of the 26- and the 21-methyl group, respectively. The 3α-hydroxyl group may well be derived from the normal 3β-group by oxidation to the ketone (still present in " β-elemonic " acid and the " normal " and " iso " masticadienonic acids), and reduction of the carbonyl to the 3α-hydroxyl group, with, in appropriate cases, isomerisation of the 7-double bond at some stage.

Flindissol may represent an intermediate biogenetic stage in the conversion of compounds containing an intact side-chain into those which, like limonin, contain a biogenetically related nucleus and have a β-substituted furan ring lacking the rest of the side-chain. Flindissol is the first substance reported which contains both the potential furan ring and the rest of the side-chain intact. Dr. T. G. Halsall has pointed out to us that further weight is lent to this hypothesis in that *Flindersia* species are related to the *Rutaceae* and *Meliaceae* which include species giving rise to a series of compounds—limonin, gedunin, khivorin, cedrolone, swietenine and nimbin—which contain a 17-3′-furyl substituent.

EXPERIMENTAL

M. p.s were determined on a Kofler block. Optical rotations were measured for chloroform, ultraviolet spectra for ethanol, and infrared spectra in carbon disulphide solutions, unless otherwise stated. Alumina refers to Spence's grade " H;" deactivated alumina was Spence's grade " H " deactivated by 3% (v/w) of 10% acetic acid. Light petroleum had b. p. 60—80°.

Isolation of Flindissol (Ia).—The milled bark of *Flindersia dissosperma* was covered with light petroleum and left for 12 hr., to remove lipids together with some flindissol which could be isolated if necessary by chromatography. Usually, this fraction was rejected and the bark then extracted (Soxhlet) with ether to give fairly pure flindissol (~3%). This was purified by chromatography on deactivated alumina in benzene–ether (1 : 1), followed by crystallisation from acetone as prismatic needles, m. p. 198°, $[\alpha]_D^{24}$ −46° (*c* 1·1), $\nu_{max.}$ 3650, 3440, 1060, 1015, and 982 cm.$^{-1}$ (Found: C, 78·7; H, 10·6. Calc. for $C_{33}H_{48}O_3$: C, 78·9; H, 10·6%). After recrystallisation from benzene it had m. p. 137°, resolidifying, remelting at 198°. In the Liebermann–Burchard test an immediate red colour rapidly became purple and then green.

The Dianhydro-dimer.—Flindissol (2 g.) in glacial acetic acid (20 ml.) was heated on the steam-bath. After 30 min. the precipitate was collected and more was obtained by evaporation of the solvent. The *dianhydro-dimer* of flindissol crystallised from chloroform–methanol as plates (1·5 g.), m. p. 315—318°, raised to 318—319° by further recrystallisation, $[\alpha]_D^{25}$ −69° (*c* 1·0), $\nu_{max.}$ 1090, 1060, 1030, 1010, and 980 cm.$^{-1}$ but no peaks above 3000 cm.$^{-1}$ [Found: C, 81·7; H, 10·6%; *M* (Rast), 926. $C_{60}H_{92}O_4$ requires C, 82·1; H, 10·6%; *M*, 876]. Ozonisation of the dimer in acetic acid, followed by decomposition of the ozonide with zinc and steam-distillation into a solution of 2,4-dinitrophenylhydrazine (0·5%) in 2N-hydrochloric acid, gave a derivative, which on recrystallisation from methanol had m. p. 122—125°, undepressed on admixture with authentic acetone 2,4-dinitrophenylhydrazone.

Hydrogenation of the anhydro-dimer (1 g.) over alkaline palladium–carbon [10b] in ethyl acetate (50 ml.) gave, on removal of the catalyst and most of the solvent, the *tetrahydrodianhydro-dimer* as plates (850 mg.), m. p. 310—312°, $[\alpha]_D^{23}$ −81° (*c* 1·09) (Found: C, 82·0; H, 10·9. $C_{60}H_{96}O_4$ requires C, 81·8; H, 11·0%).

Selenium Dehydrogenation.—Flindissol (5 g.) and selenium (6 g.) were heated under nitrogen to 320° for 4 hr., then further selenium (2 g.) was added. After a further 4 hr., more selenium (2 g.) was added and the mixture left at 320—330° for 22 hr. The cooled flask was pulverised, the whole was extracted (Soxhlet) with benzene, and the extract (2·25 g.) distilled, finally at 220—240° (bath)/0·01 mm. (757 mg.). Chromatography on Spence's grade " O " alumina in light petroleum–benzene (9 : 1) gave an oil (586 mg.), yielding a 1,3,5-trinitrobenzene adduct. Crystallisation from ethanol gave the 1,2,8-trimethylphenanthrene adduct (112 mg.), m. p. 192—193° (Found: C, 64·5; H, 4·8; N, 9·4. Calc. for $C_{23}H_{19}N_3O_6$: C, 62·7; H, 4·4; N, 9·7%). It was decomposed on alumina in light petroleum–benzene (9 : 1) to give, on recrystallisation from ethanol, colourless plates of 1,2,8-trimethylphenanthrene (55 mg.), m. p. and mixed m. p. 145—147°, $\lambda_{max.}$ 215·5, 226·6, 256, 264, 284·5, 295, 207·5, 325, 340, and 356·6 mμ (ε 24,800, 16,100, 32,500, 57,250, 9550, 8000, 9750, 450, 250, and 150).

Flindissone Lactone (Ib) *and Flindissone* (Ic).—Flindissol (2 g.) in pure pyridine (20 ml.) was added to chromium trioxide (5 g.) in pyridine (50 ml.). After working up in the usual manner, *flindissone lactone* (Ib) crystallised from ethyl acetate as prismatic needles (1·2 g.), m. p. 193—195°, $[\alpha]_D^{24}$ $-87°$ (*c* 0·93), $\nu_{max.}$ 1775 and 1710 cm.$^{-1}$ (Found: C, 79·5; H, 9·9%; *M*, 458. $C_{30}H_{44}O_3$ requires C, 79·6; H, 9·8%; *M*, 452). The molecular weight was determined by *X*-ray crystallography by Mr. O. S. Mills (Manchester) to whom we are grateful. Ozonolysis, by the procedure used for the dianhydro-dimer, gave acetone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 123—125°, *ca.* 70% yield, as the sole product. No pure compound was obtained from the non-volatile portion but the gum had $\lambda_{max.}$ 231, 238, and 247 mμ (ε ~5000).

In another experiment, *flindissone* (Ic) was obtained in about 10% yield. Recrystallisation from methanol gave needles, m. p. 147°, $[\alpha]_D^{22}$ $-45°$ (*c* 0·76), $\nu_{max.}$ 3430, 1710, and 985 cm.$^{-1}$ (Found: C, 79·3; H, 10·4. $C_{30}H_{46}O_3$ requires C, 79·2; H, 10·2%). Further oxidation of flindissone by the same method readily produced flindissone lactone, m. p. and mixed m. p. 193—195°.

Flindissone lactone was produced in 80% yield by oxidation of flindissol by 8N-chromic acid in acetone; in this case 20% of dianhydro-dimer was also produced.

Deoxyflindissol (Id) *and Deoxydihydroflindissol* (IIc).—Flindissol (1 g.) in dry ether (100 ml.) was refluxed with lithium aluminium hydride (500 mg.) for 6 hr. After working up in the standard manner, *deoxyflindissol* (Id) was obtained from acetone as prismatic needles (650 mg.), m. p. 182—185°, $[\alpha]_D^{25}$ $-34°$ (*c* 0·9), $\nu_{max.}$ 3630 and 1060 cm.$^{-1}$ (Found: C, 81·6; H, 10·8. $C_{30}H_{48}O_2$ requires C, 81·8; H, 11·0%).

Deoxyflindissol (1·65 g.) in ethyl acetate (160 ml.) was hydrogenated over alkaline palladium-carbon [10b] (300 mg.) until uptake ceased (1 mol.). Removal of the catalyst and most of the solvent gave *deoxydihydroflindissol* (IIc) as prismatic needles, m. p. 182—185°, $[\alpha]_D^{24}$ $-42°$ (*c* 1·20), $\nu_{max.}$ 3640 and 1060 cm.$^{-1}$ (Found: C, 81·7; H, 11·6. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). Acetylation of this in the usual manner gave the *acetate* as prisms (from ethyl acetate), m. p. 179°, $[\alpha]_D^{20}$ $-52°$ (*c* 1·0), $\nu_{max.}$ 1730 and 1249 cm.$^{-1}$ (Found: C, 79·1; H, 11·0. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%).

Dehydrogenation of Deoxydihydroflindissyl Acetate.—The acetate (315 mg.) in chloroform (5 ml.) was left with a 5% solution (1·7 ml.) of perbenzoic acid in chloroform for 3 days. The mixture was washed with 10% aqueous sodium hydroxide and then evaporated to a gum, $\lambda_{max.}$ 231·5, 238·5, and 247 mμ (ε 9000, 10,000, and 7000).

Dehydration of Deoxydihydroflindissol (IIc).—Deoxydihydroflindissol (500 mg.) and phosphorus pentachloride (500 mg.) were shaken in dry pentane (30 ml.) for 15 min. The mixture was washed with water, evaporated, and chromatographed on alumina in light petroleum. Recrystallisation from methanol yielded 21(23)-*epoxytirucalla*-2,7-*diene* (III) as plates (200 mg.), m. p. 104—106°, $[\alpha]_D^{25}$ $-99°$ (*c* 0·77) (Found: C, 84·6; H, 11·7. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4%).

The diene (90 mg.) was left in the dark with osmium tetroxide (250 mg.) in dry ether (3 ml.) for 5 days. Refluxing the mixture with lithium aluminium hydride and then working up in the standard manner gave a gum (90 mg.) which after careful chromatography and recrystallisation from methanol gave the 2,3-diol as prisms, m. p. 184—185°, $\nu_{max.}$ 3420, 1120, 1070, and 1050 cm.$^{-1}$. The diol (35 mg.) was treated with lead tetra-acetate in acetic acid for 24 hr. and the mixture steam-distilled into 2,4-dinitrophenylhydrazine (0·5%) in 2N-hydrochloric acid. No derivative could be extracted with benzene.

Deoxyflindissone (Ie) *and Epideoxyflindissol* (If).—Deoxyflindissol (2 g.) in dry pyridine (20 ml.) was left overnight with chromium trioxide (2 g.) in dry pyridine (20 ml.). Working up in the standard manner, followed by chromatography and recrystallisation from ether, gave *deoxyflindissone* (Ie) as prisms (1·06 g.), m. p. 168—170°, $[\alpha]_D^{23}$ $-73°$ (*c* 0·86), $\nu_{max.}$ 1708 cm.$^{-1}$ (Found: C, 81·9; H, 10·6. $C_{30}H_{46}O_2$ requires C, 82·1; H, 10·6%).

Deoxyflindissone (250 mg.) in refluxing propan-2-ol (100 ml.) was reduced by addition of small pieces of sodium (total 4 g.) during 3 hr. Working up in the standard manner, followed by chromatography on deactivated alumina in benzene, yielded needles (150 mg.) (from ether), m. p. 128—130°, $[\alpha]_D^{21}$ $-42°$ (*c* 1·0), $\nu_{max.}$ 3650, 1060m, and 1040s cm.$^{-1}$, indicating a mixture containing 75% of epideoxyflindissol (Ib) and 25% of deoxyflindissol (Id).

Reduction of flindissone lactone (If) (2 g.) in refluxing dry tetrahydrofuran (150 ml.) with lithium aluminium hydride (1 g.) for 14 hr., followed by working up in the standard manner, gave *epideoxyflindissol* (If) as prisms (1·4 g.) (from ethyl acetate), m. p. 133—135°, $[\alpha]_D^{21}$ $-48°$ (*c* 0·92), $\nu_{max.}$ 3650 and 1040 (no band at 1060) cm.$^{-1}$ (Found: C, 81·9; H, 10·8. $C_{30}H_{48}O_2$ requires C, 81·8; H, 11·0%).

Oxidation of epideoxyflindissol with chromium trioxide in pyridine as above gave deoxyflindissone (Ie), m. p. and mixed m. p. 168—170°.

Dehydration of Epideoxydihydroflindissol (IId).—Hydrogenation of epideoxyflindissol (If) (1 g.) in ethyl acetate (50 ml.) over alkaline palladium–carbon [10b] (500 mg.) yielded, after removal of the catalyst and most of the solvent, *epideoxydihydroflindissol* (IId) as prismatic needles (900 mg.), m. p. 165°, $[\alpha]_D^{26}$ $-40°$ (*c* 0·93), $\nu_{max.}$ 3650 and 1040 cm.$^{-1}$ (Found: C, 80·9; H, 11·4. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%).

Epideoxydihydroflindissol (640 mg.) was shaken with phosphorus pentachloride (650 mg.) in dry pentane (45 ml.) for 20 min. The mixture was washed with water, evaporated, and chromatographed on alumina in light petroleum, yielding an uncrystallisable gum (500 mg.) consisting of compounds (IVa) and (IVb). Ozonolysis of this gum (180 mg.) by the procedure used for the dianhydro-dimer gave eventually a precipitate shown by chromatography on paper [22] and on bentonite–kieselguhr to consist of the 2,4-dinitrophenylhydrazones of acetone (m. p. and mixed m. p. 124—126°) and formaldehyde (m. p. and mixed m. p. 165—166°) in the ratio ~4 : 1. The non-volatile portion in ether was washed with aqueous sodium carbonate solution and evaporated to a gum which had $\nu_{max.}$ 1738s and 1704m cm.$^{-1}$, indicating a mixture of cyclopentanone (from IVa) and methyl ketone (from IVb) consistent with the observed ratio of acetone and formaldehyde.

Oxidation of the dehydration product as for 21(23)-epoxytirucalla-2,7-diene (III) gave acetone and formaldehyde, again in the ratio ~4 : 1, and a neutral fraction practically identical in character with that obtained by the ozonolysis.

Acetylation of Flindissol: Acetylflindissol Lactone (Ih).—Flindissol (750 mg.) was left overnight at room temperature with acetic anhydride (5 ml.) in dry pyridine (10 ml.). Dilution with water, ether-extraction, and crystallisation from a small volume of acetone gave needles (100 mg.), m. p. 276—278°, $[\alpha]_D$ $-99°$ (*c* 1·02), $\nu_{max.}$ 1732 and 1250 cm.$^{-1}$ [Found: C, 76·3; H, 10·1. $(C_{32}H_{50}O_4)_n$ requires C, 77·0; H, 10·1%]. The nature of this compound is discussed above. The remainder of the product (650 mg.) did not crystallise but appeared to be diacetylflindissol (Ig), $\nu_{max.}$ (in CCl_4) 1740, 1728, and 1250 cm.$^{-1}$.

The gum (above) (500 mg.) in acetone (5 ml.) was oxidised by 8N-chromic acid in the usual manner. Dilution with water, ether-extraction, and recrystallisation from methanol produced *acetylflindissol lactone* (Ih) as needles (300 mg.), m. p. 198—199°, $[\alpha]_D^{22}$ $-74°$ (*c* 0·63), $\nu_{max.}$ (in CCl_4) 1783, 1740 (shoulder), 1728, and 1250 cm.$^{-1}$ (Found: C, 77·0; H, 9·5. $C_{32}H_{48}O_4$ requires C, 77·4; H, 9·7%).

Catalytic Hydrogenation of Flindissol.—(i) Flindissol (500 mg.) was hydrogenated over alkaline palladium–carbon [10b] (200 mg.) in ethyl acetate (50 ml.). After uptake had ceased (1 mol.) the catalyst and then the solvent were removed and recrystallisation from acetone gave *dihydroflindissol* (IIa) as needles (450 mg.), m. p. 150—154°, $[\alpha]_D^{25}$ $-36°$, $\nu_{max.}$ 3630 and 1060 cm.$^{-1}$ (Found: C, 78·1; H, 10·7. $C_{30}H_{50}O_3$ requires C, 78·5; H, 11·0%). Ozonolysis of this alcohol by the procedure for the dianhydro-dimer gave no volatile ketone.

(ii) Flindissol (500 mg.) in glacial acetic acid (25 ml.) was hydrogenated over Adams catalyst (500 mg.). After uptake had ceased (2 mol.) the solution was filtered and evaporated. The product, *deoxydihydroisoflindissol* (VIIa) crystallised from ethyl acetate as plates (430 mg.), m. p. 180—182°, $[\alpha]_D^{22}$ $+13°$ (*c* 0·99), $\nu_{max.}$ 3620 and 1060 cm.$^{-1}$ (Found: C, 81·5; H, 11·4. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). Ozonolysis of this product as for the dianhydro-dimer gave no volatile ketone.

(iii) Flindissol (200 mg.) in ethanol (20 ml.) and 10N-hydrochloric acid (0·1 ml.) was hydrogenated over palladium–carbon [10a] (100 mg.). One mol. was absorbed in 3 min., and 2 mol. in 30 min., then uptake ceased. Filtration and evaporation of the mixture gave a gum which produced prisms (30 mg.) from pentane; these melted at 81—83°, resolidified, and remelted at 127—135°, and had $[\alpha]_D^{20}$ $-43°$ (*c* 0·65), $\nu_{max.}$ (in Nujol) 3630, 2720, and 1708 cm.$^{-1}$ (Found: C, 81·2; H, 11·4. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). The remainder, which did not crystallise, had $[\alpha]_D^{21}$ $-29°$ (*c* 0·85), $\nu_{max.}$ (gum) 3500, 2720, and 1720 cm.$^{-1}$. The two fractions are the 20-epimers of the aldehyde (V) neither of which is known.

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[22] Horner and Kirmse, *Annalen*, 1955, **597**, 50.

Catalytic Hydrogenation of Flindissone Lactone.—(i) Hydrogenation of flindissone lactone (500 mg.) as in (i) above yielded *dihydroflindissone lactone* (IIb) as prismatic needles (450 mg.), m. p. 171—172°, $[\alpha]_D^{25}$ $-87°$ (*c* 1·15), $\nu_{max.}$ 1775 and 1710 cm.$^{-1}$ (Found: C, 78·8; H, 10·5. $C_{30}H_{46}O_3$ requires C, 79·2; H, 10·2%). Ozonolysis of this product as for the dianhydro-dimer gave no volatile ketone.

(ii) Flindissone lactone (500 mg.) was hydrogenated as in (ii) above. After uptake had ceased (2 mol.) the catalyst together with the crystalline precipitate which had been formed were filtered off and the solution concentrated to yield dihydro-α-elemonic acid (VIa) as needles (50 mg.), m. p. 275—280°. The precipitate was washed off the catalyst with chloroform and crystallised from ethyl acetate, to give further dihydro-α-elemonic acid (120 mg.), m. p. 278—282°. Recrystallisation of both fractions from ethyl acetate raised the m. p. to 289—292° (preheated block) [lit., 310° (corr.),[19] 289—291° (uncorr.) [18]]. The acid had $[\alpha]_D^{25}$ $-50°$ (*c* 0·75), $\nu_{max.}$ (in Nujol) 3400—2500, 1720, 1706, and 1665 cm.$^{-1}$ (Found: C, 78·6; H, 10·7. Calc. for $C_{30}H_{48}O_3$: C, 78·9; H, 10·6%). Treatment of the acid with ethereal diazomethane gave the methyl ester, recrystallising from aqueous methanol as needles, m. p. 160—163°, $[\alpha]_D^{23}$ $-60°$ (*c* 0·73), $\nu_{max.}$ 1735 and 1708 cm.$^{-1}$ (Found: C, 79·2; H, 10·8. Calc. for $C_{31}H_{50}O_3$: C, 79·1; H, 10·7%) (lit.,[18] m. p. 166—167°).

The mother-liquors from the hydrogenation were evaporated, and the residue, *dihydroisoflindissol lactone* (VIIb), crystallised from ether–light petroleum as blades (262 mg.), m. p. 170—172°, $[\alpha]_D^{20}$ $-38°$ (*c* 1·12), $\nu_{max.}$ 3630, 1773, and 1060 cm.$^{-1}$ (Found: C, 78·4; H, 10·7. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%). Oxidation of this with 8N-chromic acid in acetone gave *dihydroisoflindissone lactone* (VIc) as needles (from methanol), m. p. 144—146°, $[\alpha]_D^{22}$ $+28°$ (*c* 0·93), $\nu_{max.}$ 1770 and 1701 cm.$^{-1}$ (Found: C, 79·4; H, 10·2. $C_{30}H_{46}O_3$ requires C, 79·2; H, 10·2%). Ozonolysis of this lactone as above gave no volatile ketone.

(iii) Flindissone lactone (430 mg.) was hydrogenated over acidic palladium–carbon [10a] (60 mg.) in methyl acetate (50 ml.) until uptake ceased (1·4 mol.). The mixture was worked up as in (ii) above, yielding a total of 160 mg. of dihydro-" α-elemonic " acid, m. p. and mixed m. p. 288—291° (preheated block), and also dihydroflindissone lactone (260 mg.), m. p. 169—171° undepressed on admixture with compound (IIb) from (i) above.

Catalytic Hydrogenation of Acetylflindissol Lactone.—Acetylflindissol lactone (100 mg.) was hydrogenated as in (iii) for flindissol. Concentration of the filtered solution gave acetyldihydro-" α-elemolic " acid (VIb) as needles (85 mg.), double m. p. 226—230°, 234—242°, $[\alpha]_D^{20}$ $-42°$. A mixture of this and a sample prepared by hydrogenation (alkaline palladium–carbon) of authentic acetyl-" α-elemolic " acid (kindly supplied by Dr. T. G. Halsall) showed no depression of the m. p. [lit., 250—251° (uncorr.),[5] 244—245° (uncorr.) [18]].

Catalytic Hydrogenation of Isoflindissone Lactone.—Isoflindissone lactone (900 mg.) was hydrogenated as in (iii) for flindissone lactone. No precipitate was formed. Concentration of the filtered solution produced dihydro-" β-elemonic " acid (IX) as needles (350 mg.), m. p. 227—238°. Recrystallisation from ethyl acetate gave material, m. p. 232—242°, $[\alpha]_D^{14}$ $+58°$ (*c* 1·20) (Found: C, 78·5; H, 10·4. Calc. for $C_{30}H_{48}O_3$: C, 78·9; H, 10·6%) (lit., 249—250° (corr.),[19] 237—238°, clearing at 242° (uncorr.) [18]]. Treatment of the acid with ethereal diazomethane gave the methyl ester, needles (from methanol), m. p. 115—120° (lit.,[18] m. p. 112—113°).

Addition of light petroleum to the mother-liquors from the reaction mixture gave dihydroisoflindissone lactone (VIIc) as needles (460 mg.), m. p. 144—146° undepressed on mixing with material (VIIc) obtained by hydrogenation (ii) of flindissone lactone.

Catalytic Hydrogenation of Dihydroisoflindissone Lactone.—Dihydroisoflindissone lactone (200 mg.) was hydrogenated as in (ii) for flindissone lactone. Uptake ceased at 1·0 mol. Evaporation of the filtered solution and crystallisation from methanol gave dihydroflindissol lactone (90 mg.), m. p. 170—171° undepressed on admixture with the alcohol (VIIb) obtained by hydrogenation (ii) of flindissone lactone.

Reduction of Flindissone Lactone by Lithium in Ammonia.—Flindissone lactone (240 mg.) was dissolved in liquid ammonia (50 ml.) and ethanol (1 ml.). Lithium was added in thin slices so that the mixture remained blue. After 1 hr. addition of lithium was discontinued and the ammonia allowed to evaporate. The residue was taken into water and acidified, and the product was extracted with chloroform and recovered. It then contained about 25% of unchanged lactone (infrared spectrum). It was purified by repeated separation as a gel from benzene. The gel was filtered off and dried into a hard mass (170 mg.) which did not crystallise, but had $\nu_{max.}$ 3500—2400, 3350, 1715, 1665, and 965 cm.$^{-1}$. Ozonolysis of the gel as for the dianhydro-dimer gave isobutryaldehyde (m. p. and mixed m. p. 184—186°) and acetone 2,4-dinitrophenylhydrazone in the ratio ~5 : 1 (paper chromatography [22]), indicating a similar ratio of products (IX) and (X) in the gel.

The gel (120 mg.) was oxidised in the usual manner with 8N-chromic acid in acetone, and the product (110 mg.) hydrogenated over alkaline palladium–carbon [10b] in ethyl acetate (25 ml.). Filtration and concentration of the mixture gave dihydro-" α-elemonic " acid, m. p. and mixed m. p. 288—291° (preheated block).

Action of Methanolic Hydrochloric Acid on Flindissone Lactone.—(i) Flindissone lactone (150 mg.) was warmed to 40° in methanol (20 ml.) and 10N-hydrochloric acid (2 ml.) for 1 hr. and left at room temperature overnight. Evaporation gave a gum (150 mg.) which was chromatographed on deactivated alumina in light petroleum–ether. The first fraction eluted was a *keto-ester* (partial structure XII) that crystallised from methanol as leaflets (70 mg.), m. p. 128—130°, $[\alpha]_D^{22}$ $-41°$ (c 0·55), $\lambda_{max.}$ 230 (ϵ 20,500) (shoulders), 223 (ϵ 19,300), and 237 mμ (ϵ 14,500), $\nu_{max.}$ (in Nujol) 3075, 1735, 1710, 1615, 965, and 895 cm.$^{-1}$ (Found: C, 79·7; H, 9·8. $C_{31}H_{46}O_3$ requires C, 79·8; H, 9·8%). The second fraction (70 mg.) was unchanged flindissone lactone, m. p. 191—194°.

(ii) Flindissone lactone (210 mg.) was refluxed in methanol (20 ml.) and 10N-hydrochloric acid (2 ml.) for 1 hr. Evaporation gave a gum (200 mg.) which after several crystallisations from methanol gave an isomeric *keto-ester* (XIII) as needles, m. p. 160—162°, $[\alpha]_D^{22}$ $-68°$ (c 0·86), $\lambda_{max.}$ 243 (ϵ 21,000), $\nu_{max.}$ 1734, 1707, 965, and 825 cm.$^{-1}$ (Found: C, 77·8; H, 9·6. $C_{31}H_{46}O_3,CH_3{\cdot}OH$ requires C, 77·2; H, 10·0%).

Action of Methanolic Hydrochloric Acid on Dihydroflindissone Lactone.—Dihydroflindissone lactone (125 mg.) was refluxed in methanol (10 ml.) and 10N-hydrochloric acid (1 ml.) for 1 hr. Evaporation of the mixture gave a gum (125 mg.) whose infrared spectrum showed no ester absorption and whose ultraviolet spectrum showed no diene absorption. Crystallisation from methanol gave dihydroisoflindissone lactone (VIIc), m. p. and mixed m. p. 144—146°.

Other Isomerisations.—(i) *Hydrogen chloride in chloroform.*[11] A slow stream of dry hydrogen chloride was passed through a solution of flindissone lactone (1·5 g.) in dry, alcohol-free chloroform (30 ml.) at 0° for 3 hr. After being left at 0° overnight, the mixture was evaporated; the product, *isoflindissone lactone* (VII), recrystallised from methanol as needles (945 mg.), m. p. 152—153°, $[\alpha]_D^{25}$ $+38°$ (c 1·0), $\nu_{max.}$ 1772 and 1709 cm.$^{-1}$ (Found: C, 79·9; H, 9·6. $C_{30}H_{44}O_3$ requires C, 79·6; H, 9·8%).

(ii) *Adams catalyst in acetic acid.*[11] Deoxydihydroflindissol (500 mg.) was shaken with Adams catalyst (100 mg.) in glacial acetic acid (50 ml.) for 18 hr. No hydrogen was absorbed. Filtration, evaporation, and recrystallisation of the product from ethyl acetate gave deoxydihydroisoflindissol (VIIa), m. p. 180—182°, undepressed on admixture with the product of hydrogenation (ii) of flindissol.

(iii) *Sulphuric acid in acetic acid.*[3] Dihydriosoflindissone lactone (30 mg.) was heated on the steam-bath with acetic acid (5 ml.) and 2N-aqueous sulphuric acid (0·3 ml.) for 3 hr. The mixture was poured into water and extracted with ether; the extract was washed with aqueous sodium carbonate and evaporated. Recrystallisation of the product from ether–light petroleum gave a lactone (XIV) as needles (20 mg.), m. p. 168—170°, $[\alpha]_D^{22}$ $+14°$ (c 0·45), $\nu_{max.}$ (in CCl_4) 1772 and 1710 cm.$^{-1}$ [Found (3 mg. sample): C, 78·0; H, 9·8. Calc. for $C_{30}H_{46}O_3$: C, 79·2; H, 10·2%].

Epidihydroisoflindissol Lactone (VIId).—Dihydroisoflindissone lactone (600 mg.) was refluxed with sodium borohydride (500 mg.) in methanol (150 ml.) for 3 hr. and left overnight. Working up in the standard manner and recrystallisation from ethyl acetate produced *epidihydroisoflindissol lactone* (VIId) as needles (400 mg.), m. p. 205—210°, $[\alpha]_D^{20}$ $+6°$ (c 0·60), $\nu_{max.}$ (in CCl_4) 3630, 1770, and 1040 cm.$^{-1}$ (Found: C, 79·2; H, 10·3. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%).

We are indebted to the British Council (S. M.) and to D.S.I.R. (J. P. T.) for Scholarships. The bark of *Flindersia dissosperma* was supplied by the C.S.I.R.O. Phytochemical Survey. We are grateful to Dr. E. Ritchie for a gift of flindissol, to Professor C. Djerassi and Professor W. Klyne for measurements of optical rotatory dispersion, to Mr. O. S. Mills for two *X*-ray determinations of molecular weights, and to Dr. T. G. Halsall for a number of specimens of elemi acid derivatives and for some very helpful discussions.

DEPARTMENT OF ORGANIC CHEMISTRY, UNIVERSITY OF SYDNEY, AUSTRALIA.
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANCHESTER. [*Received, November 12th,* 1962.]