145. *The Chemistry of Congo Copal. Part I. Source, Properties, and Subdivision of the Raw Resin.*

By Donald A. Sutton.

The literature on the source and composition of Congo copal is reviewed. It has been found that Congo copal is a mixture of far greater complexity than had been reported and contains substances which range in molecular size from a liquid sesquiterpene to solid polycarboxylic acids of very high molecular weight. Dehydrogenation of one constituent of the resin yields 1 : 2 : 5-trimethylnaphthalene, and this compound is also obtained in a similar manner from a thermal degradation product of a second constituent. The new findings will necessitate a revision of current hypotheses with respect to the reactions which occur when the resin is heated at temperatures in the neighbourhood of 300°.

Congo copal is a fossilised natural resin used in large quantities in the manufacture of varnishes and linoleum. It is usually considered to be the standard natural resin of the varnish maker who employes it for the production of high-quality varnishes. The fossil resin is not soluble in linseed oil, and industrially it is subjected to drastic heating (*e.g.*, at 325°) in order to render it soluble so that varnishes can be prepared from it.

Congo copal is dug up by native labour in the Belgian Congo, and is washed and then graded according to colour, size, and hardness. The various grades range in appearance from transparent glass-like material to brown chips containing pieces of grit and bark. According to the standard works on natural resin technology it consists almost entirely of the fossilised product from *Copaifera Demeusei* Harms although a small percentage of the commercial resin may originate from *C. Laurentii* De Wild, *C. Arnoldiana* de Wild and *Cynometra sessiliflora*. The first is still abundant in marshy regions of the Belgian Congo, but no attempt is made commercially to obtain fresh resin by tapping living trees. The supply of fossilised Congo copal shows no sign of diminution and the existing deposits must represent a considerable tonnage.

Composition of Congo Copal.—Congo copal was originally investigated by Engel (*Arch. Pharm.*, 1908, **246**, 293; *Chem. Abs.*, 1909, **3**, 640, 1758) under the supervision of Tschirch, whose general methods were used. Resins were fractionated by treatment with solvents which dissolved out some constituents preferentially. The solutions so obtained were shaken with one of a series of aqueous alkaline solutions, *e.g.*, 1% ammonium carbonate, 1% sodium carbonate, and 1% potassium hydroxide, so as to extract the acidic components and to leave the neutral components in the solvent. Engel found 55—60% of Congo copal to be soluble in hot ether, the remainder was nearly completely soluble in ether–ethyl alcohol (1 : 1). The ethereal extract yielded an acid (50% of original copal) soluble in aqueous sodium carbonate; this acid was " purified " by conversion into the lead salt and the alcohol-insoluble portion of the latter gave a solid acid named " Congo-copalic " when treated with sulphuric acid. " Congo-copalic " acid, m. p. 115—118°, was believed to be a monocarboxylic acid of formula $C_{19}H_{30}O_2$. The non-acids in the ethereal extract consisted of a terpene, b. p. 165—166°, volatile in steam (3—4% of original copal), and " α-Congo-copal resene " (5—6% of original copal) non-volatile in steam. The ether–ethyl alcohol extract gave " Congo-copalolic " acid, $C_{22}H_{34}O_3$, m. p. 108—110° (22% of original copal), and a neutral material named " β-Congo-copal resene " (12% of original copal). Two other resins are also said to be derived from *Copaifera Demeusei* Harms, namely, Angola copal and Cameroon copal, but these have different compositions and also both differ from Congo copal according to Tschirch and Rackwitz (*Arch. Pharm.*, 1907, **245**, 423).

Bauer and Gonser (*Chem. Umschau*, 1926, **33**, 250), who re-investigated " Congo-copalic " acid, found that its molecular weight (Rast method) corresponded to $C_{38}H_{60}O_4$ and therefore stated that it was dicarboxylic. The iodine value corresponded to two double bonds per $C_{38}H_{60}O_4$ molecule. Reaction with diazomethane yielded an oily methyl ester; treatment of the acid with nitric acid gave oxalic acid and a nitrogen-containing substance $C_{38}H_{55}O_4(NO_2)_5$. Dehydrogenation with sulphur failed to yield any recognisable aromatic structure.

Mertens and Hellinckx (" Recherches sur le Copal Congo ", Brussels, 1942; *Chem. Abs.*, 1940, **34**, 3934) stated the composition of Congo copal to be: essential oils [including (—)-limonene], 5%; " Congo-copalic " acid, $C_{36}H_{58}(CO_2H)_2$, 45%; " Congo-copalolic " acid, $C_{21}H_{32}(OH)\cdot CO_2H$, 40%; " resenes ", 10%. Experimental evidence in support of this statement has not been given.

The position described is unsatisfactory from the chemical point of view and, in addition, the published information gives no clue to the reason for the excellent varnish-making properties of Congo copal.

The Congo copal used throughout the present work was, except where otherwise stated, a representative sample of the grade known as " No. 1 pale sorts "; no attempt was made to select clean or transparent pieces, except for optical tests. The refractive index and density are similar to the figures recorded by Mantell, Kopf, Curtis, and Rogers (" The Chemistry of Natural Resins," John Wiley, New York, p. 88); the resin was found to be strongly lævorotatory and to exhibit elastic recovery after being stretched whilst hot. The ether-insoluble fraction of Congo copal is also elastic when swollen with ether; these elastic properties suggested that high polymers were present and this was subsequently proved to be the case.

Carbon and hydrogen percentages are close to those required for an empirical formula of $(C_{20}H_{32\cdot2}O_{1\cdot9})_n$; hence the hydrogen/carbon ratio is appreciably higher than that of the diterpene acids of formula $C_{20}H_{30}O_2$ found in colophony. In agreement with the ratio for the total resin, a high hydrogen/carbon ratio was found for several of the main constituents.

A short examination was also carried out on the grade known as " pale ivory " which consists of opaque pieces having a milky white or pale yellow colour.

It has been found that Congo copal is a mixture of far greater complexity than appears from the literature. Seven main fractions have so far been obtained and several of these may be capable of further sub-division. Some details are given briefly in the accompanying table and the fractions are then discussed separately in more detail.

The Composition of Congo Copal.

Fraction.	Approx. percentage.	Formula based on C and H analysis, etc.	Properties.	Solubility in linseed oil.	Source.
(i) Sesquiterpene	1—2	$C_{15}H_{24}$	Liquid, b. p. 101°/3 mm.	Soluble	Ether and light petroleum extracts
(ii) Oxygen-containing neutral material	5	$(C_{16\cdot3}H_{27}O)_n$	Viscous liquid mixture of high b. p.	Soluble	Ether and light petroleum extracts
(iii) Syrupy acid, " congoic "	15	$C_{20}H_{32}O_2$ or $C_{20}H_{34}O_2$	Thick syrup giving methyl ester, b. p. 140°/0·05 mm.	Soluble; methyl ester also soluble	Ether and light petroleum extracts
(iv) Acidic material	25—30	$(C_{22\cdot6}H_{37}O_2)_n$	M. p. 70—110°, A.V.* 123. Mixture of acids not readily esterified.	Insoluble but somewhat soluble in congoic acid–linseed oil	Ether extract only
(v) Acidic material	20	$(C_{30}H_{48}O_3)_n$	M. p. 175—200°, A.V. 115. Elastic when wet with solvent. Of high mol. wt.	Insoluble	Methyl alcohol–ether extract of ether insol. portion; precipitated by addition of more MeOH
(vi) Acidic material	8	$(C_{30}H_{48}O_3)_n$	M. p. 140—165°, A.V. 115	Insoluble	Extracted as (v) but not precipitated on addition of MeOH
(vii) Totally insoluble material	20	$(C_{30}H_{48}O_3)_n$	Solid; presumably of high mol. wt.	Insoluble	Insoluble material left after extraction of fractions (i)—(vi)
Congo copal	100	$(C_{20}H_{32\cdot2}O_{1\cdot9})_n$	—	Partly soluble	Original resin

* Acid value in mg. of KOH per g. of substance.

(i) The sesquiterpene is a liquid, b. p. 101°/3 mm., $d_{4^\circ}^{25^\circ}$ 0·8933, $n_D^{25^\circ}$ 1·4935. Hence, $M[R_L]_D = 66{\cdot}4$ if $M = 204{\cdot}3$, whereas a bicyclic hydrocarbon $C_{15}H_{24}$ containing two double bonds requires 66·14. Quantitative hydrogenation at room temperature gave 2·1 double bonds per $C_{15}H_{24}$ unit. The hydrocarbon reacted with hydrogen chloride in ether at 0° to give a liquid dihydrochloride which on long standing deposited a small amount of a solid, m. p. 70—74° raised to 78—80° on recrystallisation from light petroleum. The properties of the *sesquiterpene* and its *dihydrochloride* appear to be different from those of any known sesquiterpene. The data do not prove it to be homogeneous although the boiling range was unusually narrow. The 3—4% of terpene found by Engel in the resin was not found and the (—)-limonene reported by Hellinckx is also absent unless it occurs in the small fore-run obtained on rectification of the sesquiterpene.

(ii) The material corresponding to "α-Congo-copal resene" was obtained as a viscous residue of high b. p. after the sesquiterpene had been distilled from the non-acids of the ether-soluble portion of Congo copal. The fraction contained combined oxygen and was separated into a liquid distillate and a solid residue by distillation at 10^{-4} mm., but these have not been further examined.

(iii) The diterpene monocarboxylic acid has been provisionally named "congoic" acid to avoid confusion with the acids already named by Engel. It differs from "Congo-copalic" acid since it is not a solid, and its lead salt is soluble in alcohol; it was therefore missed in Engel's fractionation of the resin. Congoic acid, unlike many resin acids, is readily esterified at room temperature with methyl alcohol containing a trace of toluene *p*-sulphonic acid. The corresponding methyl ester is a colourless liquid, b. p. 140—141°/0·05 mm., b. p. 78°/10^{-4} mm.; $d_{4^\circ}^{25^\circ}$ 0·9838, $n_D^{25^\circ}$ 1·4980. Hence, $M[R_L]_D = 94{\cdot}83$, which is close to the value 94·82 required for a bicyclic compound of formula $C_{21}H_{34}O_2$ ($M = 318{\cdot}4$) and having two double bonds; alternatively, if $M = 320{\cdot}4$ (for $C_{21}H_{36}O_2$), $M[R_L]_D = 95{\cdot}43$, whereas a bicyclic compound $C_{21}H_{36}O_2$ having one double bond requires 98·30. Carbon and hydrogen estimations are not sufficiently accurate to enable a decision to be made between $C_{21}H_{34}O_2$ and $C_{21}H_{36}O_2$ and further evidence is necessary before either can be finally accepted. The ester yielded 1 : 2 : 5-trimethylnaphthalene on dehydrogenation with selenium at 300°. Quantitative hydrogenation at room temperature gave 1·2 double bonds per $C_{21}H_{34}O_2$, and the iodine value corresponded to 0·98 double bond per $C_{21}H_{34}O_2$. The ester reacted with hydrogen chloride in ether at 0° to give a liquid *hydrochloride*, the chlorine content of which corresponded to the saturation of 1·1 double bonds per $C_{21}H_{34}O_2$. The ester thus contains one reactive double bond and may possibly contain a second double bond which is less reactive. The boiling range of the final fractionated methyl ester was narrow, but the ester has not been proved to be homogenous since all attempts to prepare solid derivatives of "congoic" acid (in order to crystallise to constant m. p.) have failed. It is hoped to report further on this acid later.

(iv) This fraction is a mixture as its indefinite m. p. indicates. It is a solid acidic material obtained in considerable amount from the ether-soluble portion of Congo copal; it should therefore consist mainly of the "Congo-copalic" acid first described by Engel. It was converted into the lead salt, which was separated into alcohol-soluble and alcohol-insoluble portions. The former represented 20% of (iv) and gave a solid acid, m. p. 140—165°, when treated with dilute sulphuric acid as described by Bauer and Gonser (*loc. cit.*); the analytical data corresponded approximately to the formula $(C_{29}H_{47}O{\cdot}CO_2H)_n$. Reaction of the *acid* with diazomethane yielded a *methyl* ester, m. p. 60—75°; *M*, 1400. This acid is thus a polymeric mixture corresponding approximately to $(C_{29}H_{47}O{\cdot}CO_2H)_3$.

The alcohol-soluble lead salt represented 80% of (iv) and gave a syrupy acid when treated with dilute sulphuric acid. Reaction of the acid with diazomethane yielded a liquid methyl ester which was fractionated under low pressure into several portions none of which was definitely homogeneous. The distillates together weighed over 80% of the crude methyl ester, and that having the highest b. p. (180—210°/0·5 mm.) was a very viscous liquid of *M*, 419.

From the results described above it is clear that the "Congo-copalic" acid described by Engel was a mixture of materials of high and of low molecular weight. These facts indicate that Bauer and Gonser were also working with a mixture which happened to give the molecular weight required for a substance of formula $C_{38}H_{60}O_4$.

(v) and (vi). These fractions are solid polycarboxylic acids and taken together they correspond to Engel's "Congo-copalolic" acid since they are extracted by methyl alcohol–ether from the ether-insoluble portion of Congo copal. Fraction (v) is precipitated from methyl alcohol–ether solution by the addition of more methyl alcohol, whereas fraction (vi) remains in solution. The analyses for (v) and (vi) correspond closely to an empirical formula of $C_{10}H_{16}O$; titration with alkali shows that approximately two-thirds of the oxygen present is in the form of free carboxyl groups and the formula must therefore be regarded as $(C_{30}H_{48}O_3)_n$. By reaction with diazomethane the *substance* (v) was converted into a white solid methyl ester. The apparent molecular weight of the methyl ester was determined at a number of concentrations in benzene solution using Gee's modification of the isothermal distillation method ("Advances in Colloid Science", **2**, 148, Interscience, New York, 1946; *Trans. Faraday Soc.*, 1946, **42**, 512;

1942, **38**, 147); extrapolation of the results to infinite dilution gave a figure of 15,400 for the number average molecular weight, corresponding to a formula for (v) of $(C_{30}H_{48}O_3)_{32}$. It is probable that (v) and (vi) are polymers of the same kind but of different average molecular weight and that neither is a single entity but represents a mixture of various molecular sizes. On heating below 200° (v) gave off a considerable amount of water. Complete fusion and rapid decomposition occurred above 350°; an oil evolved in small amount at 370° yielded 1 : 2 : 5-trimethylnaphthalene on dehydrogentation with selenium at 300°. The formation of this hydrocarbon from fractions (iii) and (v) would indicate a structural resemblance to agathic acid (Ruzicka and Hosking, *Helv. Chim. Acta*, 1931, **14**, 203) if it could be established that cyclisation has not occurred during dehydrogenation.

(vii) Carbon and hydrogen determinations on the totally insoluble fraction of Congo copal gave the same result as for (v) and (vi). None of the many solvents tried would dissolve fraction (vii), so determination of the nature and number of functional groups present has been impossible. The material swells to a jelly-like mass in some solvents and may be a cross-linked gel of " infinite " molecular weight.

Pieces of pale ivory Congo copal often have a layer of transparent material on the outside covering an inner core of translucent or opaque resin, but the author has never yet seen a sample of the resin in which the relative positions of opaque and transparent material are reversed. It is thus possible that opaque resin is slowly acted upon by atmospheric influences (*e.g.*, oxygen or light) and becomes converted into transparent resin. 32% of the sample of pale ivory Congo copal examined was insoluble (presumably cross-linked gel) as compared with 20% [fraction (vii)] in the case of No. 1 pale sorts, suggesting that a proportion of the cross-linked material becomes slowly depolymerised. Pale ivory congo copal gave very nearly the same percentages of carbon and hydrogen as No. 1 pale sorts. The ether extract was identical in amount and appeared to be essentially the same in properties as the corresponding extract from No. 1 pale sorts, but the ether-insoluble fractions of the two grades were totally different. In particular, material corresponding to fraction (v) was absent from pale ivory Congo copal whereas material corresponding to fractions (vi) and (vii) was greater in amount.

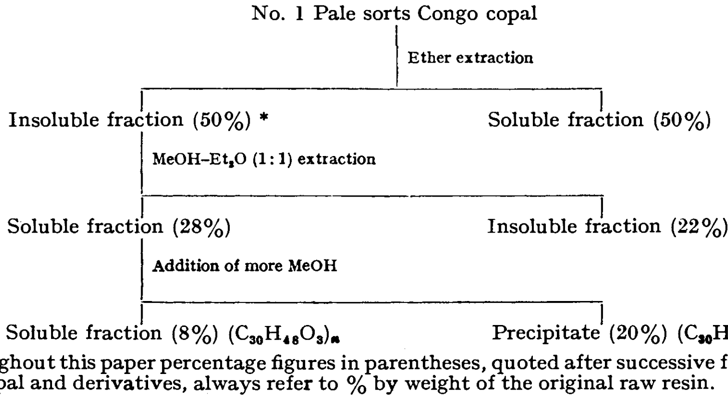
Current hypotheses relating to the reactions which occur when Congo copal is rendered soluble in linseed oil by heating at about 300° (Mantell, Kopf, Curtis, and Rogers, *op. cit.*, pp. 168—179) are based on previous literature statements about the composition of Congo copal. The fact that Congo copal contains a large proportion of a mixture of high polymers necessitates a revision of such hypotheses, and it is intended to publish a discussion of this matter elsewhere.

EXPERIMENTAL.

Properties of Congo Copal.—The resin [Found: C, 79·2, 79·4, 79·1, 79·4; H, 10·5, 10·7, 10·65, 10·75. Calc. for $(C_{20}H_{32\cdot2}O_{1\cdot91})_n$: C, 79·2; H, 10·7%] had $d_{4^\circ}^{25^\circ}$ 1·045; $n_D^{25^\circ}$ 1·536; $[\alpha]_D^{25^\circ}$ −48°; A.V., 115. Small lumps were dropped into a Banbury mixer and masticated for two hours; the warm mass showed elastic recovery after stretching.

Cold-solvent Extraction of Congo Copal.—General technique. The resin was finely powdered by a mechanical pestle and mortar and transferred to storage bottles with ground-glass stoppers (greased to prevent the access of air), all within 2 hours in order to minimise air oxidation. Extractions with solvent were carried out at room temperature in rotating bottles, 2 l. of solvent usually being used to 250 g. of resin. The solution was decanted and evaporated in pure nitrogen, the residue being finally freed from solvent in a vacuum.

Results. Solvent separation was carried out according to the scheme outlined below:



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* Throughout this paper percentage figures in parentheses, quoted after successive fractionations, etc., of Congo copal and derivatives, always refer to % by weight of the original raw resin.

Extractions were carried out by means of various solvents, the approximate percentages of the resin dissolved being :

Solvent.	Light petroleum, b. p. 40—60°.	Ether.	MeOH–Et_2O (1 : 1).	Acetone.
Percentage dissolved	22	50	80	20

It is unnecessary to give full particulars of these extractions here since the simplest method for the preliminary sub-dividion of Congo copal was found to be that in the scheme outlined above, which is described in detail below.

Ether extract. This varied in analytical constants according to the percentage of resin extracted, which depended on the amount of ether used with a given amount of raw resin ; typical figures were :

Fraction, and % extracted.	A.V.	$n_D^{25°}$.	$[\alpha]_D^{25°}$.	Description.
1st, 37%	127	1·511	−32°	Syrup
2nd, 8%	135	1·517	—	Syrup
3rd, 5%	139	—	−30	Solid of indef. m. p. *ca.* 60°
1st, 52%	130	1·514	−38	Syrup

In a typical experiment the ether extract was subdivided as follows. The extract (100 g., 40% of original copal) was stirred with warm light petroleum (1500 c.c., b. p. 40—60°) for 30 minutes. The petroleum solution was cooled and decanted from the sticky precipitate, which was dried in a vacuum to yield a white solid (A) (25 g., 10%), m. p. 70—110°. The decanted solution was washed with dilute aqueous alkali to remove the syrupy resin acid (B) (57 g., 23%), leaving in solution the neutral material (C) (17 g., 7%).

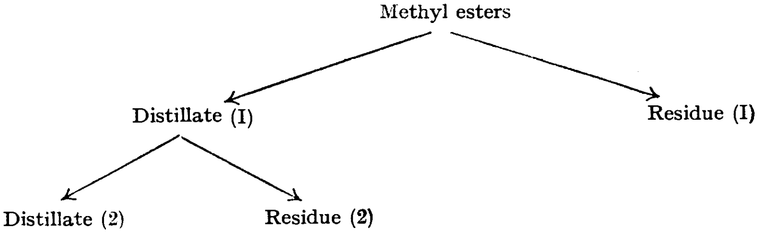
The solid (A) should correspond to a crude preparation of the " Congo-copalic " acid described by Engel and by Bauer and Gonser. A sample of (A) was converted into the lead salt as follows. The fraction (20 g.) (Found : A.V., 129, 130) was dissolved in ethyl alcohol (100 c.c.) containing acetic acid (1·5 c.c.), the solution was boiled, and a boiling solution of lead acetate trihydrate (9·3 g., *i.e.*, theoretical quantity +10%) in alcohol (100 c.c.) containing acetic acid (1·5 c.c.) was added. After standing overnight at room temperature, the supernatant solution was decanted off and the insoluble lead salt remaining was washed twice with warm alcohol (total of 65 c.c.) and dried in a vacuum ; the soluble lead salt was recovered by working up the combined filtrates.

The insoluble lead salt, which represented 20% by weight of (A), was suspended in ether (100 c.c.) in a separating funnel, and an excess of alcoholic 1% sulphuric acid was added ; after vigorous shaking, the lead sulphate was allowed to settle, and the ethereal solution was washed with water, dried, and evaporated to yield a white solid *acid* of indefinite m. p. 140—155° [Found : C, 79·4, 79·2 ; H, 10·4, 10·45 ; A.V., 133. $(C_{29}H_{47}O{\cdot}CO_2H)_n$ requires : C, 78·9 ; H, 10·6% ; A.V., 123], which was converted into the corresponding *methyl* ester, m. p. 60—75°, by reaction with diazomethane in ethereal solution containing a little ethyl alcohol [Found : *M* (Menzies–Wright, ebullioscopic in benzene), 1400. $(C_{29}H_{47}O{\cdot}CO_2CH_3)_3$ requires *M*, 1410].

The soluble lead salt, which represented 80% by weight of (A), was similarly converted into the corresponding acid, a thick syrup (Found : A.V., 129), and the latter was treated with diazomethane in ethereal solution to give an oily methyl ester which proved to be a mixture. Some of the methyl ester (10·3 g.) was fractionated at low pressure to give six distillates and a residue thus :

Fraction, and wt., g.	B. p.	$n_D^{25°}$.	Properties and appearance.
(A)i 0·4...........	165°/1 mm.	1·4938	Mobile liquid
(A)ii 2·4	167—171/1 mm.	1·4998	Mobile liquid (Found : C, 79·1, 79·4 ; H, 11·1, 11·15%)
(A)iii 0·5	171/1 mm.	1·5012	Fairly viscous liquid
(A)iv 2·3	160—170/0·5 mm.	1·5074	Viscous liquid (Found : C, 78·2, 78·1 ; H, 10·95, 10·95%).
(A)v 0·9	170—180/0·5 mm.	1·5120	Viscous liquid
(A)vi 0·8	180—210/0·5 mm.	1·5165	Extremely viscous liquid [Found : C, 77·4, 77·6 ; H, 10·8, 10, 65% ; *M* (Menzies–Wright), 419]
Residue 1·5	—	—	Dark brown solid, m. p. 49—58°

(B) is chiefly " congoic " acid, which was readily esterified and thereby separated from the bulk of the remaining " Congo-copalic " acid as follows. To the light petroleum-soluble material (B) (163·5 g.) in a 1500-c.c. conical flask were added dry methyl alcohol (1100 c.c.) and toluene-*p*-sulphonic acid (2 g.) ; the air above the solution was displaced by nitrogen, and the flask tightly stoppered. After standing for 7 days at 25°, the bulk of the methyl alcohol was quickly distilled off, water being added continuously



to keep the volume constant. The contents of the flask were poured into a separating funnel containing ether, and the remaining solid acids (46 g.) were washed out of the ethereal solution by dilute aqueous alkali, leaving the liquid methyl esters (115 g.) in solution; the latter were recovered in the usual way. The methyl esters were fractionated at 78°/10^{-4} mm. in a falling-film molecular still (Farmer and Sutton, *J. Soc. Chem. Ind.*, 1946, **65**, 164) according to the above scheme.

The fractions had the following properties :

Fraction, and wt., g.	$n_{D}^{25°}$.	$d_{4°}^{25°}$.	$[\alpha]_{D}^{25°}$.	I.V.*
Original, 27	1·5015	—	—	—
Residue (I), 6·1	1·5062	—	−40°	72
Distillate (2), 2·65	1·4982	0·9811	−31	74
Residue (2), 7·9	1·5010	0·9874	−35	78

* Iodine value (Wijs, 1 hour) as g. of iodine per 100 g. of substance.

Accumulated ester corresponding to Residue (2) above was distilled through a short column at 0·05 mm. pressure to yield :

Fraction.	B. p./0·05 mm.	$n_{I'}^{25}$.
Residue [2] (54 g.) from molecular distillation	—	1·5010
Distillate [3] (5 g.)	132—140°	1·4970
Distillate [4] (26 g.)	140—141	1·4980
Distillate [5] (14 g.)	143—148	1·4992
Distillate [6] (7 g.)	148—150	1·5000
Residue [3] (2 g.)	—	1·5100

Distillates [3] and [5] were re-fractionated at 0·05 mm. pressure to yield further amounts of b. p. 140—141° and $n_{D}^{25°}$ 1·4980, which were combined with Distillate [4] to give a colourless liquid (33 g.) as the main methyl ester fraction of " congoic " acid.

Properties of methyl ester of " congoic " acid. The ester had $n_{D}^{25°}$ 1·4980; $d_{4°}^{25°}$ 0·9838; $[\alpha]_{D}^{25°}$ −32·5° {Found: C, 79·0, 78·7; H, 11·0, 11·2; *M* (Menzies–Wright), 329, 330; I.V., 78 per double bond. Calc. for $C_{21}H_{34}O_2$: C, 79·2; H, 10·75%; *M*, 318·4. Calc. for $C_{21}H_{36}O_2$: C, 78·7; H, 11·3%; *M*, 320·4; I.V., 79·7 per double bond}.

Hydrogenation. The ester (0·8334 g.) in a mixture of methyl alcohol (50 c.c.) and pure acetic acid (5 c.c.) took up 70 c.c. of hydrogen, corresponding to the saturation of 1·2$|^{=}$ per $C_{21}H_{34}O_2$.

Hydrochlorination. Through the ester (1·0 g.) in dry ether (10 c.c.) kept at 0° was passed a great excess of dry hydrogen chloride during 90 minutes; the ether and excess of hydrogen chloride were removed in a vacuum, leaving the *hydrochloride* as a thick oil (Found : Cl, 10·7, 11·0. $C_{21}H_{35}O_2Cl$ requires Cl, 10·0%).

Dehydrogenation. The ester (3·0 g.) was heated under reflux with selenium (2·0 g.) at 300° for 2 hours; the product was distilled to give a main fraction (0·6 g.) containing 1 : 2 : 5-trimethylnaphthalene, which was identified by preparation of its styphnate, crystallised from ethyl alcohol to m. p. 129° (mixed m. p. 130° with authentic specimen * of m. p. 131°), and its picrate, crystallised from ethyl alcohol to m. p. 138—140° (Found : C, 56·85; H, 4·4; N, 10·3. Calc. for $C_{13}H_{14},C_6H_3O_7N_3$: C, 57·1; H, 4·3; N, 10·5%).

Fraction (C) was a yellow syrup which was subdivided into a distillable sesquiterpene and a residue consisting of a mixture of non-acidic oxygenated compound. A sample of (C) (33·3 g.) gave on fractionation through a short column at 3 mm. pressure : (C, i) 0·6 g., b. p. <44°; (C, ii) 6·5 g., b. p. 100—108°; (C, iii) 5·5 g., b. p. 101°; the residue was a thick syrup [Found : C, 81·9; H, 11·4. Calc. for $(C_{16\cdot3}H_{27}O)_n$: C, 82·0; H, 11·3%], corresponding to Engel's " α-Congo copal resene " (*loc. cit.*), which was heated at 150°/10^{-4} mm. in a pot-still to give a viscous liquid distillate and a solid residue. The final sesquiterpene fraction (C, iii) was obtained by redistillation of (C, ii).

Properties of the sesquiterpene. The *sesquiterpene* had the properties recorded on p. 677 and $[\alpha]_{D}^{25°}$ −10° [Found : C, 87·8; H, 11·85; *M* (Menzies–Wright), 213, 214. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%; *M*, 204·3].

Hydrogenation. The sesquiterpene (0·2437 g.) in acetic acid (25 c.c.) and in the presence of Adams's catalyst took up 56·5 c.c. of hydrogen (N.T.P.) in 25 minutes (Calc. for $C_{15}H_{24}|^{=}_{2}$: 53·5 c.c.).

Hydrochlorination. The sesquiterpene (1·0 g.) in dry ether (5 c.c.) was cooled to 0° and a large excess of dry hydrogen chloride was passed in during 75 minutes. After removal of solvent and excess of hydrogen chloride in a vacuum, the *dihydrochloride* was left as an oil (Found : Cl, 24·5, 24·8. $C_{15}H_{26}Cl_2$ requires Cl, 25·6%), $n_{D}^{25°}$ 1·5020, $d_{4°}^{25°}$ 1·055, whence, if $M = 277{\cdot}3$, $[R_L]_D = 77{\cdot}5$ (Calc. : 76·8. On long standing, this deposited a few crystals of m. p. 70—74°, raised by recrystallisation from light petroleum to 78—80°.

The ether-insoluble fraction. This swells in ether and is then elastic. In a typical experiment it was further subdivided thus : to the fraction (36 g., representing 48% of original copal) were added ether (200 c.c.) and methyl alcohol (200 c.c.); the bottle was then rolled mechanically for 12 hours. After standing for a few hours, the insoluble gel settled and the clear supernatant solution was decanted. The gel dried to a white solid (15 g., 20% of original copal), Fraction (vii) (p. 677) [Found : C, 78·85; H, 10·5. $(C_{30}H_{48}O_3)_n$ requires C, 78·9; H, 10·6%]. To each 50 c.c. of decanted solution were added 80 c.c. of methyl alcohol to cause the precipitation of a polymeric *acid* as an elastic mass which became a white powder, m. p. 175—200°, on drying [Fraction (v), p. 677], and represented 20% by weight of the original copal [Found: C, 79·1, 79·0, 78·7, 78·9; H, 10·4, 10·5, 10·6, 10·45; A.V., 115. $(C_{29}H_{47}O{\cdot}CO_2H)_n$ requires C, 78·9; H, 10·6%; A.V., 123]. The *substance* still remaining in solution was isolated and finally freed

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* Kindly supplied by Professor L. Ruzicka.

from traces of solvent, in a vacuum, and proved to be a white solid, m. p. 140—165°, *i.e.*, Fraction (vi) (p. 677) (Found: C, 78·4; H, 10·5%).

The precipitated polymeric acid. This acid, obtained by the addition of methyl alcohol to the solution as described above, was shown to contain no non-acidic material since nothing was extracted by organic solvents from an aqueous alkaline solution. It was converted into the methyl ester thus: the solid (10 g.) was dissolved in a mixture of dry ether (50 c.c.) and dry methyl alcohol (50 c.c.), an ethereal solution of diazomethane was added (*Org. Synth.*, **15**, 3) until a faint yellow colour persisted; a precipitate was formed which was removed and dried at 10^{-4} mm. to yield a white solid *methyl* ester (6·5 g.), m. p. 130—180° [Found: C, 79·7; H, 10·55; A.V., 0. $(C_{31}H_{50}O_3)_n$ requires C, 79·15; H, 10·7%; A.V., 0]; the portion of the methyl ester which had not been precipitated was obtained by evaporation as a white solid (2·7 g.), m. p. 100—130° (Found: A.V., 0). The molecular weight of the precipitated methyl ester was determined in benzene (carefully fractionated from "AnalaR" benzene) solution at seven concentrations, Gee's method (*loc. cit.*) being used; molecularly distilled linseed oil (*M*, 880) was used as the standard substance; the results were:

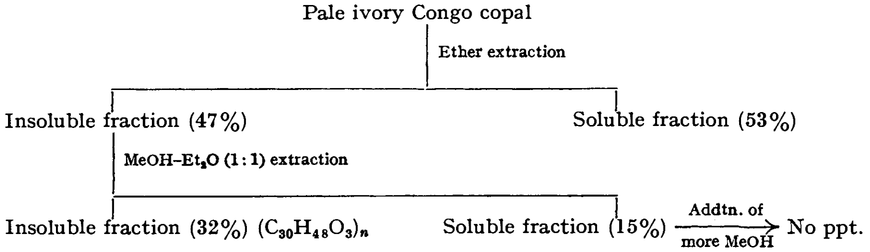
Concn. of methyl ester (g. per l. of C_6H_6)	16·4	20·7	65·5	122	125	163	195
Apparent *M*	15,600	12,900	12,300	10,820	9,650	8,170	9,160

Extrapolation of these results to infinite dilution gave 15,400 for the number average molecular weight.

Destructive distillation of the precipitated polymeric acid was first attempted by heating for 2 hours at 150—325°, followed by 1½ hours at 325—340°, but the product was not completely soluble in linseed oil at 290° although considerable decomposition had occurred. More drastic heating was used in the second attempt as follows, the product being soluble in linseed oil. The polymeric acid (20 g.) was heated in a Pyrex bulb fitted with inlet and outlet tubes which was immersed in a bath of Wood's metal kept at 350—370° for 2¼ hours during which a slow stream of pure dry nitrogen was passed through; water (>0·5 g.) and carbon dioxide (>0·02 g.) were given off, leaving a brown residue (16·1 g.) in the bulb. Some of the residue (10 g.) was dissolved in ether and divided, by washing with dilute aqueous alkali in the usual way, into solid acids of m. p. 90—120° (5·01 g.) [Found: C, 80·9, 81·1; H, 10·4, 10·3; O (by diff.), 8·7, 8·6%; A.V., 98·5, 100], and viscous liquid non-acids (3·5 g.).

The non-acids were heated in a vacuum to give a liquid distillate (0·5 g.), b. p. 122—126°/2 mm., which was dehydrogenated by heating with selenium at 300° for 12 hours; the total dehydrogenation product was heated in ethyl alcohol (1 c.c.) containing picric acid (0·1 g.), and on cooling, red needles of a picrate crystallised out which were recrystallised to m. p. 139—140° (mixed with an authentic specimen of 1 : 2 : 5-trimethylnaphthalene picrate of m. p. 140°, m. p. 139—140°).

Pale Ivory Congo Copal.—The resin (Found: C, 79·6, 79·7, 79·5, 79·3; H, 10·4, 10·5, 10·8, 10·7%) was finely powdered, and subdivided by solvents in a similar way to that described above for the other copal, as in the scheme below:



The ether extract appeared to be similar in amount and properties to the corresponding extract from No. 1 pale sorts:

Ether extract from:	Resin, %.	A.V.	$n_D^{25°}$.	$[\alpha]_D^{25°}$.
Pale ivory	53	120	1·517	−30°
No. 1 pale sorts	52	130	1·514	−38

The ether-insoluble fraction contained a white solid (15%) (Found: 77·7, 77·5; H, 10·5, 10·5%) which was soluble in methyl alcohol–ether; none of this was precipitated on addition of further methyl alcohol to the solution. The totally insoluble residue (32%) [Found: C, 78·7, 79·1; H, 10·6, 10·75. Calc. for $(C_{30}H_{48}O_3)_n$: C, 78·9; H, 10·6%] was more than the corresponding fraction of No. 1 pale sorts.

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