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RHODESIAN TEAK TANNIN

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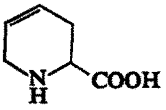
Abstract—An examination of the tannin from Rhodesian teak (*Baikiaea plurijuga*) heartwood suggests that it is principally an anhydropolyleucofisetinidin. The property of the timber of turning red when exposed to light is associated with this constituent.

Hederagenin and pinitol were also isolated as heartwood constituents in addition to the already known baikiain.

INTRODUCTION

Rhodesian teak (*Baikiaea plurijuga*) is a hard durable timber used in the U.K. mainly for flooring. The freshly cut timber has a straw-brown colour which quickly reddens on exposure to light and air, though after a prolonged period of exposure this redness is lost and the wood assumes a mature brown hue. These changes, which are clearly chemical in origin, prompted us to re-examine the extractive constituents in an attempt to isolate and characterize the compounds concerned. From previous work Rhodesian teak is known to contain *ca.* 1 per cent of an amino acid—baikiain (I)[1]—and *ca.* 10 per cent of a tannin[2]—probably a complex leucoanthocyanidin[3]—and it is this latter substance which is probably associated with the reddening of the wood in light.



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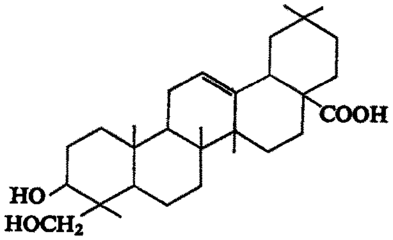

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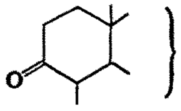

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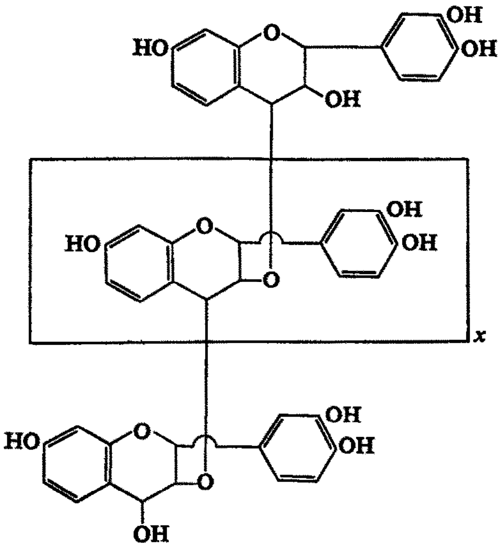

(IV)

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[1] F. E. King, T. J. King and A. J. Warwick, *J. Chem. Soc.* 3590 (1950).

[2] E. W. H. Rottsieper, *Vegetable Tannins*, p. 71. Forestal Land Timber and Railways Co. (1947): published for private circulation. Report of The Forest Products Research Board for 1950, p. 45. H.M.S.O. (1951).

[3] D. G. Roux, *Nature* **180**, 973 (1957).

RESULTS AND DISCUSSION

In the present investigation the wood dust was extracted successively with boiling light petroleum, ether, acetone and methanol which removed 0·2, 0·2, 17 and 14 per cent of extractives respectively (based on the air-dry weight of wood). From the ether extract a dihydroxytriterpene acid $C_{30}H_{48}O_4$ was isolated which was shown to be hederagenin (II). The compound was characterized through its methyl ester, methyl ester diacetate, and bromolactone and on pyrolysis it gave formaldehyde and the known nor-ketone (III). The identity was finally confirmed by comparison with an authentic sample.

The solution obtained by acetone extraction was concentrated, and evaporation of an aliquot afforded a phenolic syrup which was completely insoluble in ether and failed to give any crystalline phenolic products. However, the deep red solutions produced on treatment with hydrochloric acid in propanol indicated the probable presence of leucoanthocyanidins.[4] The major portion of the concentrated acetone extract on keeping at room temperature for several months deposited a small quantity of D-pinitol.

The crude leucoanthocyanidin gave no crystalline derivatives and showed no discrete spots on paper chromatography, so further characterization was carried out on the crude product defined by its isolation procedure. In this the water-soluble part of the acetone extract was extracted by ethyl acetate and the leucoanthocyanidin was recovered from this solution by precipitation with ether. To minimize the amount of impurity in this fraction the initial extraction of the wood dust was carried out using cold acetone and care was taken not to expose the extract unduly to heat, light or air. A sample prepared by repeated precipitation was obtained as a hygroscopic buff powder which contained no methoxyl groups, and which gave a red colour with the vanillin reagent, a green colour with ferric chloride and a colourless precipitate with gelatin. The powder showed the reddening on exposure to light typical of the wood. Paper chromatography of the anthocyanidin produced by acid treatment gave a red spot at R_f 0·70 (AcOH:H_2O:HCl) subtended by an intense red streak from the origin; in addition an orange-yellow spot was observed at higher R_f. The position of the red spot corresponds to that expected for pelargonidin or fisetinidin and a choice in favour of the latter can be made as the red anthocyanidin solution (λ_{max} 530 nm) became blue (λ_{max} 573 nm) on addition of aluminium chloride.[5] Synthetic fisetinidin prepared by King and White's method[6] behaved similarly whilst synthetic perlagonidin showed no shift with aluminium chloride.

Dry distillation of the substance afforded a mixture of phenols which when separated by thin-layer chromatography was seen to consist mainly of resorcinol and catechol. Furthermore alkali fusion gave a phenolic fraction from which resorcinol was isolated as its benzoate, and an acidic fraction which afforded protocatechuic acid characterized as its acetate. In addition the acid fraction yielded a small amount of *p*-hydroxybenzoic acid. The degradation products and the anthocyanidin produced by acid treatment are in agreement with the tannin consisting mainly of a polyleucofisetinidin, but the isolation of *p*-hydroxybenzoic acid indicates the presence of another component possibly based on a 4′,7-dihydroxyflavan-3,4-diol structure.

The chromatographic behaviour of the polyleucofisetinidin, together with its tannin properties suggests that it is of an intermediate molecule weight range and it is thus similar to the tannins which occur in black wattle (*Acacia mearnsii*) heartwood,[7] and quebracho

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[4] W. PIGMAN, E. ANDERSON, R. FISCHER, M. A. BUCHANAN and B. L. BROWNING, *Tappi* **36**, 4 (1953).

[5] H. H. KEPPLER, *J. Chem. Soc.* 2721 (1957).

[6] H. G. C. KING and T. WHITE, *J. Chem. Soc.* 3901 (1957).

[7] D. G. ROUX and E. PAULUS, *Biochem. J.* **80**, 476 (1961), **82**, 320 (1962); D. G. ROUX, *Chem. Ind.* 278 (1962).

(*Schinopsis* spp). heartwood.[8, 9] These tannins are also based mainly on polyleucofisetinidin and are considered to derive from the co-occurring monomeric 3′,4′,7-trihydroxyflavan-3,4-diols. The wattle heartwood affords (+)-3′,4′,7-trihydroxyflavan-3,4-diol[5] whilst the (−)-isomer is obtained from quebracho wood.[10] By a combination of countercurrent and paper chromatography techniques Roux has isolated fractions of the wattle heartwood tannin corresponding to monomer, trimer, pentamer, and decamer; the crystalline monomer 3′,4′,7-trihydroxyflavan-3,4-diol was first isolated by Keppler[5] and the amorphous polymeric fractions, which have similar chemical properties, can be distinguished by their mobility on paper chromatograms (R_f's (in BuOH : H_2O) 0·60 (monomer), 0·42 (trimer), 0·20 (pentamer)). The Rhodesian teak tannin was not separated into fractions in this way but the streaks obtained on paper chromatography (R_f 0·15–0·88, most intense in region 0·42–0·71) suggest that the substance has a similar molecular weight distribution. However, the optimum yield (2·0 per cent) of anthocyanidin from Rhodesian teak tannin, calculated from the optical absorption[9] is lower than the yields from the wattle tannin fractions (4·78–6·75 per cent).[7]

The tannin gave an amorphous acetate and an amorphous methyl ether. The methyl ether was subdivided into two main fractions and one smaller fraction but none of these were obtained crystalline. The analyses of these products were in agreement with a polyleucofisetinidin structure based on $nC_{15}H_{14}O_6-(n-1)\,H_2O$ and molecular weights on the methyl ether fractions suggested that n is of the order 3–5. The NMR spectra of the methyl ether fractions showed no absorption in the region τ 7·0 (associated with the methylene group at C-4 in flavan-3-ols)[11] indicating the probable absence of any catechin type polymer.

The analyses of the methyl ether acetates obtained by acetylation of the methyl ether fractions also agreed with the above formulation and these had a methoxyl–acetyl molecular ratio of about 6:1. As the method of methylation was specific for phenolic hydroxyl groups and as the subsequent acetylation of the remaining alcoholic hydroxyl groups was complete (no hydroxyl bands in the i.r. spectra) this is also the ratio of phenolic to alcoholic hydroxyl in the tannin polymer. In 3′,4′,7-trimethoxy-3,4-diacetoxyflavan the methoxyl–acetyl ratio is 3:2, and in a polymer in which only one of the alcoholic hydroxyls is involved in each link this ratio would increase to no more than 3:1. If the Rhodesian teak tannin is considered to be composed entirely of trihydroxy-flavan-diol units it must be concluded from the observed ratio of 6:1 that both alcoholic hydroxyls are involved in the linkage with acetylation occurring only at the terminal hydroxyls (e.g. as in (IV)). The value found suggests an average degree of polymerization of four units, which agrees with the molecular weight evidence for the methyl ethers. On the basis of the foregoing evidence it is tentatively suggested that Rhodesian teak tannin consists mainly of an anhydropolyleucofisetinidin $nC_{15}H_{14}O_6\text{-}(n-1)$ H_2O where $n=3$–5 for a major portion, and which is probably linked through the 3 and 4 hydroxyl groups. Analysis of the crude tannin agreed with this formulation although the C-values were somewhat higher than anticipated owing to the presence of less oxygenated components (viz. isolation of *p*-hydroxybenzoic acid).

Roux has discussed the reddening of flavan-3,4-diol based tannins, particularly with regard to those derived from wattle, and has shown that this property is associated with the 7- and 4-hydroxyl groups of the polyleucoanthocyanidins present.[12] In compounds containing a 5-hydroxyl group in addition, this reddening tendency is enhanced. The light-induced

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[8] D. G. Roux, *Nature* **181**, 1454 (1958).

[9] D. G. Roux and S. R. Evelyn, *Biochem. J.* **69**, 530 (1958).

[10] D. G. Roux, *Chem. Ind.* 161 (1958).

[11] J. W. Clark-Lewis, L. M. Jackman and T. M. Spotswood, *Australian J. Chem.* **17**, 632 (1964).

[12] D. G. Roux and S. E. Drewes, *Chem. Ind.* 1442 (1965).

reddening of Rhodesian teak is thus accounted for by the presence of the leucofisetinidin polymer. The marked degree to which reddening occurs in this wood may indicate that small amounts of other 5-hydroxyl compounds are present but no chemical evidence was obtained in support of this.

Examination of the methanol extract gave only the previously known constituent—baikiain. This was isolated by warm-acid treatment of the water-soluble part which served to polymerize and render insoluble any water-soluble phenolic impurities. The crude baikiain hydrochloride obtained was recrystallized from *n*-propanol and from the propanol mother liquors a small amount of an artefact was isolated which was shown by synthesis to be the propyl ester of baikiain hydrochloride.

EXPERIMENTAL

Melting points were determined in open Pyrex tubes except where designated s.e.t. (sealed evacuated tube): specific rotations were measured at room temperature.

Hot extraction of Rhodesian teak. Freshly prepared sawdust (6·4 kg) was extracted for successive 18-hr periods with boiling light petroleum, ether, acetone and methanol in a continuous return copper extractor. The petroleum extract was evaporated to a thin amber oil (13·1 g) and the ether extract afforded a light brown amorphous solid (13·1 g). On shaking the ether extract with methanol, crude hederagenin (5·2 g) remained undissolved. The acetone extract was concentrated to 2 l.; 200 ml of this solution when evaporated gave 110 g of a brown syrup. The remaining 1800 ml on standing several months at room temperature deposited crystals of D-pinitol (3·7 g), m.p. and mixed m.p. 189–191°, $[\alpha]_D+66°$ (*c*, 1 in H_2O) (identity confirmed by i.r. comparison).

The methanol extract was evaporated to 2 l.; 100 ml evaporated to dryness gave 44·4 g dark brown syrup. Another 1400 ml was evaporated to dryness and shaken with water (2 l.). Conc. HCl (400 ml) was added to the filtered aqueous solution and the mixture was kept at 100° for 1 hr. Precipitated solid (224 g) was filtered off and the filtrate was evaporated to a residue which crystallized on treatment with ethanol. The crude baikiain hydrochloride (100 g) thus obtained was recrystallized from *n*-propanol to give 67 g, m.p. 268–270°, $[\alpha]_D-146°$ (*c*, 1 in H_2O) (lit.[1, 13] m.p. 264°, $[\alpha]_D-153°$). A small portion of the crude product which did not dissolve during the recrystallization was recrystallized from methanol to give inactive baikiain hydrochloride (1·3 g), m.p. 268–270°. The residue (13·1 g) obtained on evaporation of the *n*-propanol mother liquors was extracted with boiling acetone. On concentrating the acetone solution granular prisms were obtained of the *n-propyl ester of baikiain hydrochloride* (2·7 g), m.p. 173·5–174·5°, $[\alpha]_D-116{\cdot}4°$ (*c*, 1 in H_2O). (Found: C, 52·3; H, 7·7; N, 6·6. $C_9H_{16}O_2NCl$ required: C, 52·5; H, 7·8; N, 6·8%) on recrystallization from ethanol–acetone. The compound sublimed at 110° *in vacuo*. A synthetic sample prepared by boiling baikiai hydrochloride (2·0 g) with *n*-propanol (100 ml) and concentrated HCl (1 ml) for 2 hr was identical with the above compound by mixed m.p. and i.r. comparison.

Cold Acetone Extraction of Rhodesian Teak

Sawdust (1·5 kg) was extracted for 18 hr with boiling ether and then three times by soaking in cold acetone overnight (3 × 3 l.). The combined acetone solutions were evaporated to a brown glass (193 g) which was leached with cold water. The filtered aqueous solution was extracted with ethyl acetate and the ethyl acetate solution on evaporation gave a dark brown glass which solidified on trituration under ether. The product (100 g) obtained was the crude tannin investigated below.

Hederagenin. The triterpene when recrystallized from methanol–chloroform had m.p. 333–335° (s.e.t.), 324–327° decomp. (open tube), $[\alpha]_D+68°$ (*c*, 0·5 in dioxan), +78° (*c*, 1 in pyridine), ν_{max} (mull) 1685 cm^{-1}. (Found C, 76·0; H, 10·2 Calc. for $C_{30}H_{48}O_4$: C, 76·3; H, 10·2%.) Lit.[14, 15] m.p. 332–334°, $[\alpha]_D+80°$ (pyridine), +71·4° (MeOH–$CHCl_3$). The compound gave a positive Liebermann–Burchardt reaction, was acidic and did not depress the melting point of an authentic sample of hederagenin; the i.r. spectra were identical. The bromolactone prepared under King, King and Ross's conditions[16] had m.p. 218–220° decomp. $[\alpha]_D+71{\cdot}4°$ (*c*, 1 in $CHCl_3$). Lit.[15, 17] m.p. 226–228°, $[\alpha]_D+72{\cdot}5°$ ($CHCl_3$).

Hederagenin, methyl ester. The methyl ester obtained by diazomethane methylation, on recrystallization

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[13] F. E. KING and T. J. KING, *Chem. Ind.* 489 (1953).

[14] W. A. JACOBS, *J. Biol. Chem.* **64**, 379 (1925).

[15] A. WINTERSTEIN and G. STEIN, *Z. Physiol. Chem.* **211**, 5 (1932).

[16] F. E. KING, T. J. KING and J. M. ROSS, *J. Chem. Soc.* 1333 (1955).

[17] A. WINTERSTEIN and J. MEYER, *Z. Physiol Chem.* **199**, 37 (1931).

from aqueous methanol, had m.p. 235–238° (s.e.t.), $[\alpha]_D + 75°$ (c, 1 in $CHCl_3$), ν_{max} ($CHCl_3$) 1710 cm^{-1}. Lit.[18] m.p. 238–240°, $[\alpha]_D + 75°$ (EtOH).

Two crystalline forms of the methyl ester diacetate, m.p. 139° (from aqueous methanol) and 192–194, (from light petroleum), $[\alpha]_D + 79°$ (c, 1 in $CHCl_3$), ν_{max} ($CHCl_3$) 1710 cm^{-1} were obtained. Lit.[15,19] m.p. 192°, $[\alpha]_D + 75{\cdot}3°$ ($CHCl_3$).

A mixture of methyl ester (0·2 g) and copper bronze (0·6 g) when heated at 280° for 20 min under a current of N_2 at 90 mm gave methyl hederagone, m.p. 201–203°, $[\alpha]_D + 105°$ (c, 1 in $CHCl_3$), ν_{max} ($CHCl_3$), 1700 cm^{-1}. Lit.[20] m.p. 203°, $[\alpha]_D + 105°$ ($CHCl_3$). The issuing gases when passed through dimedone solution precipitated the formaldehyde–dimedone complex, m.p. and mixed m.p. 189·5–191·5°.

Rhodesian Teak Tannin

The tannin isolated from the acetone extract was dissolved in cold ethanol and passed through a short polyamide column. The eluate on evaporation gave a residue which was dissolved in ethyl acetate and then poured into excess light petroleum. The precipitated tannin was obtained as a pale buff hygroscopic amorphous powder $[\alpha]_D - 28{\cdot}1°$ (c, 0·6 in MeOH) λ_{max} 281 nm $E^{1\%}_{1\,cm}$ 189. (Found (for a sample dried at 110° *in vacuo*): C, 67·6; H, 5·0. $nC_{15}H_{14}O_6 - (n-1)H_2O$ required, for $n=3$: C, 64·7; H, 4·6 and for $n=5$: C, 65·2; H, 4·5%.) The compound gave a deep red colour with vanillin–HCl,[21] a green colour with ethanolic ferric chloride and a colourless precipitate with the gelatin reagent.[22]

When chromatographed on paper in *n*-butanol (saturated with water) and sprayed with toluene-*p*-sulphonic acid the tannin appeared as a continuous streak from R_f 0·15 to 0·88 which was more intense in the region 0·4–0·7; 2% acetic acid also produced a streak R_f 0–0·46.

Conversion to the anthocyanidin. The optimum yield of fisetinidin chloride was obtained by heating the tannin (40 mg) with *iso*-propanol-3 N HCl (10 ml, 5:1) for 75 min in a sealed tube at 100°.[4] Paper chromatography of the derived anthocyanidin gave a red spot at R_f 0·70 (AcOH:H_2O:HCl, 30:10:3) which was subtended by an intense red streak from the origin, and a yellow spot at R_f 0·75. A portion of the above red solution diluted 1 in 10 ml with ethanol had λ_{max} 530 nm. A further 1 ml of the solution was evaporated and 5 ml of 1% ethanolic $AlCl_3$ was added; the blue solution made up to 25 ml with ethanol had λ_{max} 573 nm. The separated red spot from the chromatogram had λ_{max} 526 nm shifted to 567 nm by the addition of $AlCl_3$. Synthetic fisetinidin chloride[6] had λ_{max} 526 nm shifted to 570 nm on adding $AlCl_3$, whilst synthetic pelargonidin chloride, λ_{max} 532 nm, was unaffected by $AlCl_3$.

One millilitre of the above anthocyanidin solution (from Rhodesian teak tannin) was diluted to 50 ml with *iso*-propanol and had an absorbance of 0·218 at 532 nm (1 cm cell). Using the value given by Roux[9] for the absorption of pure fisetinidin chloride this corresponds to a yield of 2·0% anthocyanidin from the tannin.

Acetate. Treatment of the tannin with acetic anhydride and pyridine at room temperature or at the boiling point gave an acetate which was reprecipitated from methanol as an amorphous colourless solid, $[\alpha]_D - 3{\cdot}2°$ (c, 1·5 in $CHCl_3$). (Found: C, 62·00; H, 4·6; Ac, 36·0. Trimer $C_{45}H_{27}O_{16}(Ac)_{11}$ required: C, 62·0; H, 4·67; Ac, 36·5. Pentamer $C_{75}H_{45}O_{26}(Ac)_{17}$ required: C, 62·5; H, 4·6; Ac, 34·9%.)

Degradation of the Tannin

Pyrolysis. The tannin (10 g) was heated in a hard glass tube under N_2 and the volatile products (*ca.* 2 ml) were collected in a solid CO_2 trap. The product was examined by TLC on silica using benzene–dioxan–acetic acid (90:25:4) as a developing agent. On spraying the plate with vanillin–HCl an intense red spot R_f 0·52, and a smaller blue spot, R_f 0·66, appeared. Resorcinol and phloroglucinol markers gave red spots R_f 0·52 and 0·29 respectively. A second plate was sprayed with ethanolic ferric chloride giving a single green spot at R_f 0·55; catechol and pyrogallol markers gave a green spot at R_f 0·55 and a purple spot at R_f 0·41 respectively.

Alkali fusion. The tannin (5 g) in a mixture of KOH (10 g), NaOH (10 g) and water (5 ml) was heated to 180–200° for 10 min under N_2. The cooled melt was diluted with water, acidified with HCl and extracted with ether. The product was separated by aq. $NaHCO_3$ into phenolic (1·1 g) and acidic (2·1 g) components in the usual way; both fractions contained crystalline material. A portion of the phenolic fraction was chromatographed on TLC and using the above spray reagents resorcinol was identified as the main constituent. Other weaker spots were not identified. A quantitative estimation of the constituents from the thin-layer plate showed that at least 25 per cent of the phenolic fraction was resorcinol. A further portion (1 g) of the phenolic fraction was chromatographed on a silica column. Fractions eluted by ether were then rechromatographed on another silica column in benzene. Elution with benzene–ether (1:1) gave crystalline resorcinol; benzoate m.p. and mixed m.p. 114·5–116·5° by Schotten–Baumann procedure.

Examination of the acid fraction by thin-layer chromatography showed it to be a complex mixture. A

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[18] W. A. Jacobs, *J. Biol. Chem.* 63, 621 (1925).

[19] Z. Mustafa and G. Soliman, *J. Chem. Soc.* 70 (1943).

[20] K. Tsuda and S. Kitegawa, *Chem. Ber.* 71, 1604 (1938).

[21] D. E. Hathway and J. W. T. Seakins, *J. Chem. Soc.* 1562 (1957).

[22] D. McCandlish, *Tannin Analysis*, p. 5, A. Harvey, Croydon (1942).

preliminary purification was effected by passing a solution in benzene–ether (1:1) through a column of silica. The eluted fractions were then separated by preparative TLC on silica in benzene–dioxan–H_2O (90:25:4) using double development. Four main fractions, R_f 0·65 (65 mg), 0·49 (255 mg), 0·21 (14 mg) and 0·11 (45 mg), were removed from the plate. Acetylation of the first fraction gave *p*-acetoxybenzoic acid (30 mg), m.p. and mixed m.p. 193–195°. The second fraction on acetylation gave protocatechuic acid diacetate (90 mg), m.p. and mixed m.p. 161–162·5°; no other substances were isolated from this fraction but the presence of compounds based on resorcinol was indicated as the crude fraction gave the colour reactions of both *m*-dihydroxy (vanillin–hydrochloric acid) and *o*-dihydroxy (ferrous sulphate–sodium bicarbonate) groups.

Methylation of tannin. A solution of the tannin (5 g) and dimethyl sulphate (17·5 g) in acetone (300 ml) containing anhydrous K_2CO_3 (25 g) was boiled with stirring for 5 hr. The filtered reaction mixture was evaporated and treated with 50% NH_4OH. The product, recovered in $CHCl_3$, was a syrup which was dissolved in hot methanol. A fraction, A (1·52 g), was deposited as a crisp powder on cooling and the methanol-soluble part was recovered and chromatographed on a column of alumina in benzene. Elution by benzene and ether gave only traces of syrup but elution by acetone gave a colourless amorphous solid, B (1·82 g). Further elution with methanol gave another fraction, C (0·50 g). Each fraction was prepared for analysis by precipitation from methanol solutions by pouring into ether. There were no detectable differences between the i.r. spectra of the three products. Methyl ether A had $[\alpha]_D$ −12·9° (*c*, 1·7 in $CHCl_3$) (Found: C, 67·6; H, 5·95; OMe, 31·3%; M.W. (Rast) 1400); methyl ether B had $[\alpha]_D$ − 16·1° (*c*, 1·6 in $CHCl_3$) (Found: C, 67·6; H, 6·1; OMe, 31·2%; M.W. (Rast) 920); methyl ether C had $[\alpha]_D$ −29·8° (*c*, 1·4 in $CHCl_3$) (Found C, 65·7; H, 6·1; OMe, 30·0%; M.W. (Rast) 750). The trimer $C_{45}H_{29}O_7(OMe)_9$ requires C, 67·5; H, 5·9; OMe, 29·1%; M.W. 960 and the pentamer $C_{75}H_{47}O_{11}(OMe)_{15}$ requires C, 68·0; H, 5·8; OMe, 29·3%; M.W. 1588.

Acetylation of each methyl ether at room temperature using acetic anhydride–pyridine gave amorphous acetates which were prepared for analysis by precipitation from methanol solution by pouring into water. The compounds analysed as follows: The acetate of A (Found: C, 67·2; H, 6·0; OMe, 30·0; Ac, 6·4%); the acetate of B (Found: C, 66·7; H, 5·9; OMe, 29·5; Ac, 6·6%) and the acetate from C (Found: C, 66·4; H, 6·0; OMe, 28·8; Ac, 7·0%). The trimer $C_{45}H_{27}O_7(OMe)_9(Ac)_2$ requires C, 66·6; H, 5·8; OMe, 26·7; Ac, 8·2% and the pentamer $C_{75}H_{45}O_{11}(OMe)_{15}(Ac)_2$ requires C, 67·4; H, 5·8; OMe, 27·8; Ac, 5·1%.

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