997. *Extractives from Woods. Part II.** *Extractives from* Vitex divaricata.

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The heartwood of *Vitex divaricata* (black fiddlewood) contains esters and their long-chain alcohols and acids in which the C_{30} compounds predominate.

A number of species of *Vitex* (family Verbenaceae) have already been investigated. The twigs and leaves of *V. trifolia*[1] contain α-pinene, camphene, and terpinyl acetate, whilst the leaves of *V. negundo*[2] contain (—)-sabinene, *p*-hydroxybenzoic acid, protocatechuic acid, 5-hydroxyisophthalic acid, and gluconontrile. *V. littoralis*[3,4] and *V. peduncularis*[5] contain vitexin.[4,6] We have found that *V. divaricata* contains waxes and their acids and alcohols, triacontan-1-oic acid and tricontan-1-ol being predominant. Vitexin has not been found.

Extraction of the heartwood with ligroin gave neutral and acid fractions. The acid fraction, which was saturated, was purified by ion-exchange chromatography and then had m. p. 85—87°. Its infrared spectrum suggested long-chain fatty acids and the melting point corresponded with that of hexacosanoic acid. Its methyl ester, m. p. 73—74°, was, however, found by gas–liquid chromatography, to be a mixture of hexa- and octa-cosanoate and tria- and dotria-contanoate in which the triacontanoate preponderated.

The neutral fraction contained long-chain alcohols and esters, which were separated into the two groups by chromatography on alumina. The alcohol fraction had melting point and composition corresponding to triacontan-1-ol. Conditions for direct analysis by gas–liquid chromatography were not found, but the composition of the alcohol fraction was established in two ways. (*a*) The fraction was oxidised to an acid mixture which was esterified and the composition of the mixture was established by gas–liquid chromatography. The alcohol fraction was thus shown to contain traces of octadecan-1-ol, eicosan-1-ol, docosan-1-ol, and pentacosan-1-ol and larger quantities of octacosan-1-ol, triacontan-1-ol, and dotriacontan-1-ol. Triacontan-1-ol constituted nearly 90% of the mixture. (*b*) The acetates of the alcohols were submitted to gas–liquid chromatography and the presence of the acetates of eicosan-1-ol, docosan-1-ol, octacosan-1-ol, and triacontan-1-ol (90%) was detected. The traces of C_{18}, C_{20}, C_{22}, and C_{25} alcohols were not on this occasion detected. The acetate of dotriacontanol may have been too firmly bound on the column under the conditions of analysis.

The ester fraction was saponified and the acid fraction formed was analysed by gas–liquid chromatography of its methyl esters. The alcohol fraction formed was similarly analysed as its acetate. In this way the acid fraction was shown to consist of a mixture of octacosanoic, triacontanoic, and dotriacontanoic acid, in which the C_{30} acid was predominant. The alcohol fraction was shown to consist of a mixture of octacosan-1-ol and triacontan-1-ol, the latter predominant. The extractive of *Vitex divaricata* thus consists very largely of triacontanyl triacontanoate and the corresponding acid and alcohol.

Experimental

Chromatographic analyses were performed on the Aerograph HY-FI instrument (Wilkens Instrument & Research, Inc.).

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* Part I, *J.*, 1962, 4906.

[1] Shinozaki, *J. Chem. Ind., Japan*, 1921, **24**, 191.

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[4] Evans, McGookin, Jurd, Robertson, and Williamson, *J.*, 1957, 3510.

[5] Sharma, *J. Sci. Ind. Res., India*, 1955, **14**, *B*, 267; *Chem. Abs.*, 1956, **50**, 5649.

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The heartwood of *Vitex divaricata* (2360 g.) was extracted continuously with ligroin (b. p. 60—80°; 10 l.) for 90 hr., the mixture cooled, and the white solid (13·5 g.) collected. Concentration of the extract to 3 l. afforded solid (15 g.), and complete removal of solvent gave a brown syrup (8 g.) which afforded further solid (5·5 g.) as residue when distilled in steam. The solids were combined and fractionated as follows. Amberlite resin IRA-400 was converted into its carbonate form. The above solid (1·5 g.), dissolved in a hot mixture of ethanol (500 c.c.) and ethyl acetate (50 c.c.), was added slowly in portions to the stirred resin (30 g.) kept at 70° and stirring was continued for 10 min. after addition of each portion of solid. The supernatant liquid was decanted and the resin was washed with ethanol at 70° until no more solid appeared on evaporation of the solvent. The combined washings and supernatant liquid gave a neutral fraction (0·8 g.), m. p. 79—81°. The resin was then washed with 1 : 20 formic acid–ethanol, giving an acid fraction (0·5 g.), m. p. 85—87° (lit.: [7] hexacosanoic, m. p. 87·7°, heptacosanoic, m. p. 87·5—87·7°, octacosanoic, m. p. 90·9°, triacontanoic acid, m. p. 93·6°).

Acid Fraction.—No change in m. p. was effected after several crystallisations of this fraction from ethanol or ligroin. It showed peaks (in Nujol) at 2680 (CO_2H), 1710 (CO_2H), 732, and 715 cm.$^{-1}$ (chain of CH_2 groups) (Found: C, 78·8; H, 13·1. Calc. for $C_{28}H_{56}O_2$: C, 79·2; H, 13·3. Calc. for $C_{29}H_{58}O_2$: C, 79·4; H, 13·3. Calc. for $C_{30}H_{60}O_2$: C, 79·6; H, 13·4%). The acids (35 mg.) were suspended in freshly made ethereal diazomethane for 48 hr. and the esters (36 mg.) were collected and crystallised from methanol and then from ethyl acetate, giving a product, m. p. 73—74°, $\nu_{max.}$ 1748 (ester), 1510, 1170 (ester), 732 and 715 cm.$^{-1}$ (Found: C, 79·1; H, 13·0. Calc. for $C_{29}H_{58}O_2$: C, 79·4; H, 13·3. Calc. for $C_{31}H_{62}O_2$: C, 79·8; H, 13·4%). The esters were chromatographed under conditions shown in Table 1.

TABLE 1.

Composition of the mixture of methyl esters from the free acids, m. p. 85—87°.

Column, Silicone S.E. 30; 275° ± 1°; chart speed 20 in./hr.; N_2 flow 25 c.c./min.; H_2 flow 21 c.c./min.

Peak no.	Relative retention time (Me docosanoate = 1)	Retention vol. (c.c.)	Fatty acids (as Me esters)	Approx. quantity (%)
1	0·41	41·3	Octadecanoic	Authentic specimen
2	0·62	63·8	Eicosanoic	,, ,,
3	1·0	101·3	Docosanoic	,, ,,
4	1·68	168·8	Tetracosanoic	,, ,,
5	2·74	236·0	Hexacosanoic	0·04
6	4·44	442·5	Octacosanoic	4·2
7	7·97	761·2	Triacontanoic	84·3
8	11·65	1140·0	Dotriacontanoic	4·2

Neutral Fraction.—This fraction, m. p. 79—81° (1·34 g.), dissolved in warm dry benzene (150 c.c.), was adsorbed on a column of neutral alumina (94 cm. × 2·5 cm.; 310 g.) and eluted (*a*) with benzene-ether (9 : 1), giving esters (66 mg.), and (*b*) with ether–methanol (7 : 3), giving free alcohols (0·5 g.).

(i) *Free-alcohol fraction.* This was crystallised first from ligroin and then from ethyl acetate, forming plates, m. p. 84° (triacontan-1-ol melts at 86·5° [8]), $[\alpha]_D$ 0°, $\nu_{max.}$ 3340 (OH), 1053 (OH), 732, 715 cm.$^{-1}$ (chain of CH_2 groups), with a succession of bands between 1175 and 1150 cm.$^{-1}$ (Found: C, 82·0; H, 14·7%; *M*, 420. Calc. for $C_{29}H_{60}O$: C, 82·0; H, 14·2%; *M*, 424. Calc. for $C_{30}H_{62}O$: C, 82·1; H, 14·2%; *M*, 438). The corresponding acetate, crystallised first from ethyl acetate and then from acetone, was deposited as plates, m. p. 68—70° (triacontanyl acetate has m. p. 73° [9]), $\nu_{max.}$ 1745 (ester), 1236 (OAc), 1047 cm.$^{-1}$ (Found: C, 80·1; H, 13·0. Calc. for $C_{31}H_{62}O_2$: C, 79·8; H, 13·4. Calc. for $C_{32}H_{64}O_2$: C, 79·9; H, 13·4%). Chromatography of the acetates is recorded in Table 2. The phenylcarbamate, m. p. 97—98° (phenylcarbamate of triacontan-1-ol has m. p. 96° [10]), consisted of needles (when crystallised in succession from acetone, methanol, and ligroin), $\nu_{max.}$ 3333 (NH), 1695 (amide) 1653, 1600 cm.$^{-1}$ (Found: C, 79·1; H, 11·9. Calc. for $C_{36}H_{65}NO_2$: C, 79·5; H, 12·0. Calc. for $C_{37}H_{67}NO_2$: C, 79·7; H, 12·0%). The 3,5-dinitrobenzoate, crystallised successively from ligroin, ethanol, and acetone, formed needles, m. p. 84·5°, $\nu_{max.}$ 1754 (ester), 1639 (aryl), 1550 and 1176 cm.$^{-1}$

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[9] Shriner, Nubenhauer, and Anderson, *J. Amer. Chem. Soc.*, 1927, **49**, 1290.
[10] Heiduschka and Gareis, *J. prakt. Chem.*, 1919, **99**, 310.

TABLE 2.

Composition of the mixture of acetates of the free alcohols.

Column, Silicone S.E. 30; 276° ± 1°; chart speed 20 in./hr.; N_2 flow 25 c.c./min.; H_2 flow 21 c.c./min.

Peak no.	Relative retention time (eicosanyl acetate = 1)	Retention vol. (c.c.)	Alcohols (as acetates)	Approx. quantity (%)
1	1	63·8	Eicosan-1-ol	Trace
2	1·56	105	Docosan-1-ol	,,
3	6·33	420	Octacosan-1-ol	6
4	9·95	660	Triacontan-1-ol	90

(ester) (Found: C, 69·9; H, 10·2. Calc. for $C_{35}H_{60}N_2O_6$: C, 69·5; H, 10·0. Calc. for $C_{37}H_{64}N_2O_6$: C, 70·2; H, 10·2%).

The mixture of alcohols (48 mg.) in acetone (distilled from permanganate; 20 c.c.) was refluxed for 3 hr. with a solution of chromium trioxide (2·56 g.) in sulphuric acid (2·3 c.c.) and water (8 c.c.), and then cooled. The acids (42 mg.), deposited as a white solid, crystallised from ethyl acetate, giving an amorphous solid, m. p. 86—87°, $\nu_{max.}$ 1695 (CO_2H), 940, 715, and 732 cm.$^{-1}$ (Found: C, 78·7; H, 13·0. Calc. for $C_{28}H_{56}O_2$: C, 79·2; H, 13·3. Calc. for $C_{30}H_{60}O_2$: C, 79·6; H, 13·4%). The methyl ester, made with fresh diazomethane in methanol–ether, crystallised from acetone in needles, m. p. 71—72°, $\nu_{max.}$ 1754 (ester), 1176 (ester), 732, and 715 cm.$^{-1}$. This was submitted to gas–liquid chromatography, as detailed in Table 3.

TABLE 3.

Composition of the mixture of methyl esters obtained by oxidation of free-alcohol mixture.

Column, Silicone S.E. 30; 275° ± 1°; chart speed 20 in./hr.; N_2 flow 25 c.c./min.; H_2 flow 21 c.c./min.

Peak no.	Relative retention time (Me docosanoate = 1)	Retention vol. (c.c.)	Fatty acids (as Me esters)	Approx. quantity (%)
1	0·35	37·5	Octadecanoic	Trace
2	0·58	63·8	Eicosanoic	,,
3	1·0	105·0	Docosanoic	,,
4	1·97	210·0	Pentacosanoic	,,
5	4·08	433·5	Octacosanoic	3
6	6·81	723·8	Triacontanoic	88
7	10·58	1125·0	Dotriacontanoic	3

(ii) *Esters.* This fraction, crystallised from acetone, had m. p. 66—68°, $\nu_{max.}$ 1745 and 1174 (ester), 732, and 715 cm.$^{-1}$ (chain of CH_2 groups). It (109 mg.) was refluxed with potassium hydroxide (0·5 g.) in methanol (10 c.c.) and benzene (10 c.c.) for 65 hr. Water was then added, the mixture was stirred, and the aqueous layer was extracted with warm ether. Solvent was removed from the combined ether and benzene solutions, and the residue was heated at 80° with acetic anhydride (1 c.c.) and pyridine (1 c.c.) for 12 hr. This gave a mixture of acetates (41 mg.) which crystallised from methanol as needles, m. p. 72—74°,[9] $\nu_{max.}$ 1738 (ester), 1248 (OAc), 1040, 730, and 720 cm.$^{-1}$ (CH_2) (Found: C, 80·0; H, 13·3. Calc. for $C_{32}H_{64}O_2$: C, 79·9; H, 13·4%). Its composition as found is shown in Table 4.

TABLE 4.

Composition of the mixture of acetates of the ester alcohols.

Column, Silicone S.E. 30; 278° ± 1°; chart speed 20 in./hr.; N_2 flow 32 c.c./min.; H_2 flow 22 c.c./min.

Peak no.	Relative retention time (eicosanyl acetate = 1)	Retention vol. (c.c.)	Alcohols (as acetates)	Approx. quantity (%)
1	1	74·8	Eicosan-1-ol	Authentic
2	1·53	115·2	Docosan-1-ol	,,
3	6·21	595·2	Octacosan-1-ol	14
4	10·00	979·2	Triacontan-1-ol	85

Acidification of the aqueous alkaline solution last mentioned gave an acid (102 mg.), m. p. 83—86°, which was dissolved in ethanol and passed several times through the carbonate form of " Ionenaustauscher III " (Merck). The resin was then washed with 1 : 20 formic acid–ethanol, giving an acid fraction (26 mg.), m. p. 90°, $\nu_{max.}$ 1700 (CO_2H), 1290, 940 (CO_2H), 730, and 720 cm.$^{-1}$. This (18 mg.) was esterified with diazomethane, giving an ester, m. p. 66—68°, $\nu_{max.}$ 1750 (CO_2R), 1170 (CO_2R), 880, and 720 cm.$^{-1}$, whose chromatography is recorded in Table 5.

All the chromatographic separations (Tables 1—5) were repeated on a silicone–rubber column, which was somewhat more polar than the S.E. 30 column. The compositions of the various mixtures were confirmed. Conditions of separation on more polar columns could not be found.

The ligroin-extracted wood (2500 g.) was continuously extracted with methanol, from which lignin (80 g.) was obtained. This was stirred with water (200 c.c.) and filtered off, yielding insoluble lignin (20 g.). The aqueous solution of lignin was concentrated to 100 c.c., concentrated hydrochloric acid (1 c.c.) was added, and the mixture was refluxed for 3 hr. The solution was chromatographed on paper [solvent system: pyridine (40 c.c.), ethyl acetate (160 c.c.), water (20 c.c.)] with glucose as standard [spray: phthalic acid (3·3 g.), aniline (20 c.c.), acetone (95 c.c.), water (5 c.c.)]. A single spot (R_G 1) of glucose was developed.

TABLE 5.

Composition of the acids obtained by saponification of the esters.

Conditions of chromatography as in Table 1.

Peak no.	Relative retention time (docosanoate = 1)	Retention vol. (c.c.)	Fatty acids (as Me esters)	Approx. quantity (%)
1	4·41	438·7	Octacosanoic	12
2	7·71	757·5	Triacontanoic	84
3	11·68	1132·0	Dotriacontanoic	2·5

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