CLXXI. THE WAX OF WHITE PINE CHERMES¹

By BERTIE KENNEDY BLOUNT, ALBERT CHARLES CHIBNALL
AND HOSNI AHMED EL MANGOURI

*From the Dyson Perrins Laboratory, South Parks Road, Oxford, and the
Biochemical Department, Imperial College of Science and
Technology, South Kensington*

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A PRELIMINARY examination of the wax of white pine chermes, *Adelges (Pineus) strobi* Börner, has been reported by Blount [1936], who found that it was similar to, but not identical with, that of cochineal [Chibnall *et al.* 1934], consisting of a ketonic alcohol esterified by a ketonic acid. The components of cochineal wax are 15-keto-*n*-tetratriacontanol (cocceryl alcohol) (II), 13-keto-*n*-dotriacontanoic acid (III) and *n*-triacontanoic acid; those of the white pine chermes are now shown to be 17-keto-*n*-hexatriacontanol (I), 11-keto-*n*-triacontanoic acid (IV) with a negligible amount of what may be *n*-fatty acid.

It will be seen that the new ketonic alcohol is the next higher even-number homologue of cocceryl alcohol, and the ketonic acid the next lower even-number homologue of that in cochineal, all four substances possessing in common the group $\text{CH}_3 \cdot (\text{CH}_2)_{18} \cdot \text{CO}$ and fitting neatly into the scheme of metabolism of waxes put forward by Chibnall & Piper [1934].

The chain length of the two new products was foretold at once by X-ray analysis, and as before, their constitution has been determined by putting the oximes of the respective ketonic acids through a Beckmann transformation and hydrolysing the resulting mixed amides. In the case of the naturally occurring ketonic acid an elegant separation of the resulting products was effected by simple extraction with four different solvents in succession, *n*-eicosanoic acid, *n*-nonane-1:9-dicarboxylic acid, *n*-nonadecanamine hydrochloride and 10-amino-*n*-decanoic acid hydrochloride being thus obtained in excellent yields. The amides derived from the ketonic alcohol via the ketonic acid, however, were found to be unexpectedly difficult to hydrolyse and the separation of the resulting products was less complete; *n*-eicosanoic acid, *n*-pentadecane-1:15-dicarboxylic acid and *n*-nonadecanamine hydrochloride being obtained in reasonable yields, but only a trace of the expected 16-aminopalmitic acid hydrochloride.

EXPERIMENTAL

Saponification of the wax

The preparation of the purified wax has already been described [Blount, 1936]. 14.5 g. were dissolved in 200 ml. of hot benzene, 700 ml. of 5% alcoholic KOH were added and the mixture boiled under reflux for 12 hr.; 500 ml. of

¹ The melting-points of the ketonic acids and ketonic alcohol recorded in this paper were obtained by the method described by Piper *et al.* [1931].

95% alcohol containing 70 g. CaCl_2 were then added and the boiling continued for another 2 hr. The procedure then followed that of Chibnall *et al.* [1934], which included a second saponification with sodium ethoxide. It is doubtful, however, if this latter operation was necessary, as the "residual unsaponified wax" consisted very nearly, if not entirely, of ketonic alcohol, whose solubility in the extracting solvents (boiling alcohol and boiled acetone) was lower than had been anticipated. The yield of ketonic alcohol, m.p. 102–102.5°, was 5.6 g. and of the ketonic acid, m.p. 103–104°, was 5.5 g.

Constitution of the ketonic acid

The ketonic acid was digested for some time with 1.5 l. of boiling acetone, filtered on a hot funnel and the filtrate kept at 37° overnight. The material (5 g.) crystallized in fine rhombic leaflets. A sample recrystallized from acetone at 37°, melted sharply at 103.3–103.6° and gave an X-ray picture (series B, 484) with 17 orders measuring 80.65 Å. showing that the chain length was C_{30} . (Found: C, 77.25; H, 12.65%. $\text{C}_{30}\text{H}_{58}\text{O}_3$ requires C, 77.2; H, 12.5%.) 4.5 g. of the acid were oximated, and a very small amount of crude *n*-fatty acid (0.36 g.; m.p. 78°) separated by fractional crystallization [cf. cochineal ketonic acid, Chibnall *et al.* 1934]. The purified oxime (3.6 g.) melted at 62.5°.

3.5 g. of this material were converted into the corresponding amides by heating with pure H_2SO_4 (20 ml.) for 1 hr. on a water-bath. The dark thick solution was then poured on to crushed ice, the precipitated material collected and crystallized from 200 ml. of glacial acetic acid. After drying *in vacuo* over NaOH overnight the amides (2.86 g.) were obtained as a greyish powder melting at 105°. These were hydrolysed by heating with 15 ml. of conc. HCl in a sealed tube at 180° for 4 hr. The resulting dark brown products were taken to dryness *in vacuo*, the hard waxy substance thus produced powdered as finely as possible with a sharp knife and then extracted four times successively (filtering hot) with 20 ml. of boiling light petroleum (b.p. 40–60°). The extracts were colourless, and on removal of the solvent gave a hard white mass (0.8 g.) of *n*-eicosanoic acid. Crystallized once from acetone at 30° it melted at 74.8–75.0°, unchanged when mixed with the synthetic acid. (Found: mol. wt. by titration, 313. $\text{C}_{20}\text{H}_{40}\text{O}_2$ requires 312.)

The residue from the petroleum treatment, after removal of traces of solvent, was extracted repeatedly at room temperature with ether until no more material dissolved. The colourless ethereal extracts, on removal of the solvent, gave 0.48 g. of a hard white product melting above 100°. This was taken up in 200 ml. of boiling water, and a small amount of molten *n*-fatty acid removed by filtration. The water-clear filtrate on cooling at 0° gave 0.4 g. of crystalline *n*-nonane-1:9-dicarboxylic acid; m.p. 110.5–111°, unchanged when mixed with the synthetic acid. (Found: C, 61.0; H, 9.3%; mol. wt. by titration (dibasic acid), 217. $\text{C}_{11}\text{H}_{20}\text{O}_4$ requires C, 61.0; H, 9.3%; mol. wt. 216.)

The residue from the above treatment was next extracted repeatedly with benzene, the mixture being warmed to 65–70° and filtered hot. The benzene extracts on cooling at 0° gave 0.63 g. of brownish crystalline material. As this might contain a small amount of the ω -amino-acid hydrochloride it was dissolved in 20 ml. of warm absolute alcohol and treated with 0.4 ml. of 5 *N* NaOH to convert the amine hydrochloride into the free base. Water was then added and the free base extracted with ether. The ethereal solution was evaporated, the residue taken up in 20 ml. of warm alcohol, decolored with charcoal and acidified with conc. HCl. Ether (2 vol.) was then added to the warm solution, and on keeping overnight at 0° 0.51 g. of *n*-nonadecanamine hydrochloride crystallized out. (Found: C, 71.1; H, 13.3; N, 4.2%. $\text{C}_{19}\text{H}_{41}\text{N HCl}$ requires C, 71.3; H, 13.2;

N, 4.4 %.) The benzoate melted at 88°, alone and when mixed with the benzoate of the synthetic amine.

The final residue (0.45 g.) was taken up in 20 ml. of boiling *N* HCl, filtered hot, the filtrate decolored with charcoal and left overnight at 0°. The crystalline deposit of 10-amino-*n*-decanoic acid hydrochloride was removed by filtration, and the mother-liquor, on concentration *in vacuo* over NaOH, yielded a second crop of colourless plates. The material, 0.2 g. in all, melted at 159°. (Found: N, 6.5 %. $C_{10}H_{21}O_2N \cdot HCl$ requires N, 6.3 %.) The free amino-acid was prepared by dissolving 0.1 g. of the hydrochloride in the calculated volume of 0.1 *N* NaOH. A white crystalline mass separated on cooling in the ice chest, which was filtered off, washed and recrystallized from 10 ml. of boiling water. The large thin plates thus obtained melted at 187.5–188°; Blaise & Houillon [1906] give 187–188°. (Found: C, 64.0; H, 11.2 %. $C_{10}H_{21}O_2N$ requires C, 64.1; H, 11.3 %.)

Constitution of the ketonic alcohol

The alcohol, on crystallization from chloroform, melted at 102.5–102.8°. The X-ray photograph (series B, 466) gave 17 orders measuring 96.42 Å. showing that the chain length was C_{36} . (Found: C, 80.4; H, 13.5 %. $C_{36}H_{72}O_2$ requires C, 80.5; H, 13.5 %.) The acetyl derivative melted at 84.2° and the oxime at 78.5°.

4 g. of the alcohol, on oxidation with CrO_3 (cf. cocceryl alcohol [Chibnall *et al.* 1934]) gave 3.2 g. of purified ketonic acid, m.p. 107.5–108°, and 3 g. of this acid gave 2.1 g. of purified oxime, m.p. 67°. After the Beckmann transformation 1.8 g. mixed amides, m.p. 108° were obtained. These were hydrolysed with 7 ml. of conc. HCl for 4 hr. at 180°, but the product, when put through the above-mentioned separation, yielded only 0.134 g. of *n*-fatty acid and 0.1 g. of crude dicarboxylic acid. The residue was therefore again hydrolysed, this time with double the volume of HCl for 8 hr. at 180°, but even so the subsequent fractionation showed that the hydrolysis was incomplete.

The combined light petroleum extracts yielded in all 0.234 g. of *n*-eicosanoic acid; m.p. 74.8–75°, unchanged when mixed with synthetic acid. (Found: mol. wt. by titration, 313. $C_{20}H_{40}O_2$ requires 312.) The ethereal extracts, on treatment as in the former case, gave 0.1 g. of dicarboxylic acid, melting at 115° and of mol. wt. 328, showing that unchanged amides were present. These were removed in the following way. The material was titrated in alcoholic solution to phenolphthalein with alcoholic KOH, the alcohol removed and the dry potassium salt transferred to a small centrifuge tube. 5 ml. of cold water were then added, the mixture stirred and the insoluble residue centrifuged off. The clear solution of potassium soap was then run slowly, with vigorous stirring, into 600 ml. of boiling water containing a small excess of HCl. The separated dicarboxylic acid was collected and the purification repeated. *n*-Pentadecane-1:15-dicarboxylic acid (32 mg.) crystallized from the boiling solution in small needles; m.p. 116.5–117° (Chuit [1926] gives 118°). (Found: C, 68.1; H, 10.7 %; mol. wt. by titration (dibasic acid), 298. $C_{17}H_{32}O_4$ requires C, 68.0; H, 10.7 %; mol. wt. 300.)

Extraction of the residue from the petroleum treatment with hot benzene gave 0.862 g. of brown material. When this was taken up in 30 ml. of absolute alcohol and 0.6 ml. of 5*N* NaOH was added a heavy precipitate was thrown down. This was filtered off and the filtrate treated as in the previous case. 0.11 g. of *n*-nonadecanamine hydrochloride was obtained, which was characterized as its benzoate, m.p. 88°. The alcohol-insoluble sodium salt was converted into the free acid by heating with glacial acetic acid containing 5 % HCl, the

mixture thrown into water and the precipitated acid filtered off. This was crystallized from alcohol (charcoal), and 0.46 g. of colourless crystalline material was obtained. It melted at 110°, with a mist that cleared at 117°, and undoubtedly consisted in large part of unchanged amides (mol. wt. by titration 559).

The residue from the hot benzene treatment, on extraction with 15 ml. of boiling *N* HCl yielded a very small amount of brownish material melting at 158°, probably an impure sample of the expected 16-aminopalmitic acid hydrochloride.

SUMMARY

The wax of white pine chermes (*Adelges (Pineus) strobi* Börner) is composed of a ketonic alcohol (17-keto-*n*-hexatriacontanol) esterified by a ketonic acid (11-keto-*n*-triacontanoic acid). The two products are thus the next higher and next lower even-number homologues respectively of the ketonic alcohol and ketonic acid present in cochineal (*Coccus cacti*) wax, all four substances possessing the common group $\text{CH}_3 \cdot (\text{CH}_2)_{18} \cdot \text{CO}$.

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