

## Constituents of the Wood of *Juniperus communis* L.

JOHAN B-SON BREDEBERG and JARL GRIPENBERG

*Department of Chemistry, Institute of Technology, Helsingfors, Finland*

The neutral part of the extract of the wood of *Juniperus communis* L. contains, in addition to the previously reported sugiol, a substance which most probably is a mixture of ferruginol and some closely related compound, and also a yellow compound termed xanthoperol. Xanthoperol appears to be an artefact and a partial structure is suggested.

We have previously<sup>1</sup> reported the presence of sugiol in the wood of the common juniper (*Juniperus communis* L.). Although this work dealt primarily with the phenolic part of the extract, it could be demonstrated that sugiol occurred also in the neutral part.

A more thorough investigation of this neutral part has now been made. It was divided by steam distillation into a volatile and non-volatile fraction, and it is the investigation of the latter, which forms the subject of the present paper.

This fraction, which amounted to 1.8 % of the air-dried wood, was hydrolysed with alcoholic potassium hydroxide after preliminary experiments had shown that direct chromatography gave no useful results. The acids obtained in the hydrolysis were mainly fatty acids and no separation of them was attempted. The high equivalent weight of a crude preparation indicated, however, the presence of considerable amounts of acids higher than stearic acid.

The unsaponifiable part was chromatographed giving as a first fraction a thick oil, this being followed by two colourless crystalline compounds and finally a yellow compound.

The oil showed absorption at 280 m $\mu$ , indicating the presence of a phenol. Further attempted purification by chromatography followed by acetylation failed to give any crystalline material. However, vacuum distillation of the oil gave fractions from which a crystalline acetate could be obtained. This analysed for C<sub>22</sub>H<sub>32</sub>O<sub>2</sub>, corresponding to the composition C<sub>20</sub>H<sub>30</sub>O for the parent phenol. Hydrolysis of the acetate gave the phenol as an only partially crystalline material, which indicates that it is a mixture. As there is no reason to believe that the hydrolysis has caused any change in the phenol it can be assumed that even the acetate is a mixture, in spite of the fact that it behaves as a pure compound. The properties of both the acetate and the free phenol

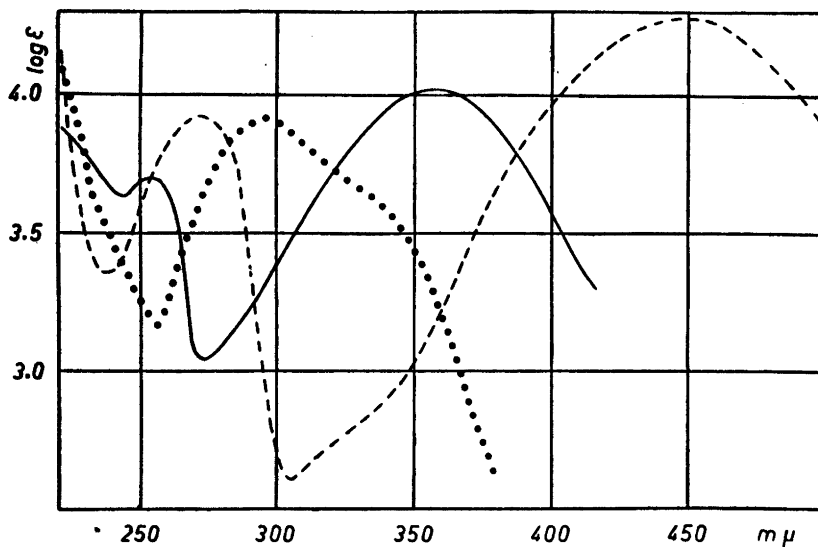


Fig. 1. Ultraviolet absorption curves of (—) xanthoperol in ethanol, (---) xanthoperol in 0.05 N sodium carbonate and (... ..) xanthoperol acetate.

are rather close to those of ferruginol (I), previously isolated from the wood of some conifers<sup>2</sup>, suggesting that the present material is a mixture of ferruginol with some other closely related compound, most probably the corresponding dehydroderivative.

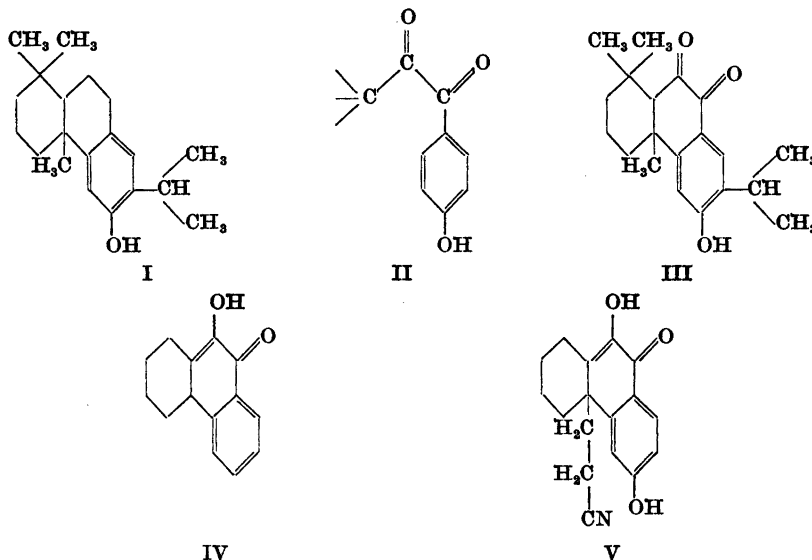
The two colourless compounds that are eluted from the chromatogram in the following fractions have been identified as sugiol and  $\beta$ -sitosterol.

The compound, which was most strongly absorbed on the column was obtained as yellow needles and melts between 255 and 270° with decomposition. It is optically active, with  $[\alpha]_D^{20} +132,5^\circ$  (ethanol) and has the composition  $C_{20}H_{26}O_3$ . The name xanthoperol is proposed for this apparently new compound. The nature of the three oxygen atoms can be deduced from the infra-red spectrum. This shows peaks at 3 436, 1 717 and 1 658  $cm^{-1}$ , which can be attributed to a hydroxyl not involved in a chelate ring formation, an unconjugated ketone in an open chain or a six membered ring and a conjugated ketone, respectively. Further bands at 1 595, 1 567 and 1 502  $cm^{-1}$  are attributed to an aromatic ring. A band at 883  $cm^{-1}$  indicates the presence of isolated hydrogen atoms in the aromatic ring.

The presence of a hydroxyl group is further demonstrated by the formation of an acetate. That the hydroxyl is phenolic is shown by the large hypsochromic effect of acetylation and bathochromic effect of alkalinisation on its U.V. spectrum (see Fig. 1). This last mentioned shift ( $\sim 90 m\mu$ ), taken together with the infra-red evidence presented above, points to the presence of a carbonyl group in the *p*-position to the phenolic hydroxyl, although the shift is even larger than those usually given by this grouping<sup>3,4</sup>. The *pK*-value, which is lower than 8.5 is also in agreement with the presence of such a grouping. The

yellow colour indicates either a 1,2-diketone or a quinone. The latter is, however, incompatible with the infra-red absorption in the carbonyl region.

The facts mentioned above lead to the proposal of the partial structure (II), where the aromatic ring must carry at least two substituents in such positions that there are no adjacent hydrogen atoms.



The obvious extension of this to the complete formula (III) must be regarded with some doubt, because such a structure ought to exist mainly in the enolic form. Parham *et al.*<sup>5</sup> have synthesised the compound IV and Gates<sup>6</sup> the compound V. In neither case is there any evidence for the presence of the diketone form.

That xanthoperol does not exist as such in the wood can be seen from the fact that no yellow zone corresponding to that of xanthoperol is observed when chromatographing the material before hydrolysis. This has also been confirmed by a spectrophotometric investigation of fractions obtained in this way. There was in no fraction any selective absorption at 350  $m\mu$  in neutral or at 450  $m\mu$  in alkaline medium, characteristic of xanthoperol. After hydrolysis certain fractions showed these maxima, indicating that xanthoperol had been formed.

Experiments are in progress aimed at establishing the structure of xanthoperol and its precursor, as well as the nature of the ferruginol-like mixture.

#### EXPERIMENTAL

(All m.p.s are determined on a Kofler microscope. The microanalyses have been performed by Dr. A. Bernhardt, Mülheim.)

*Separation of the compounds.* The non-steam volatile portion of the neutral extract<sup>1</sup> was dissolved in ethanol and heated on a water bath with 2 N potassium hydroxide for 2 h. The ethanol was evaporated in a stream of carbon dioxide and water and ether were added. A gelatinous precipitate was thereby formed. The aqueous phase gave, after acidification and recrystallisation from methanol, a mixture of acids, m.p. 61–64°, equiv. wt. 308.

The precipitate and the ether soluble part were chromatographed separately but found to yield essentially the same results. Chromatography was carried out on standardised alumina using light petroleum as solvent and light petroleum-ether mixtures followed by ether as eluent, the appropriate fractions being combined.

Light petroleum eluted a comparatively large amount of a non-crystalline material. Ether-containing light petroleum eluted first sugiol, followed by a sterol, and finally the yellow xanthoperol. The last mentioned came out just before changing to ether as eluent. Further elution with ethanol-containing ether or pure ethanol failed to give any recognisable substances.

The non-crystalline light petroleum eluate (36.2 g) was distilled under vacuum. After a forerun boiling at 94–185°/0.2 mm, two main fractions b.p. 175–185°/0.15 mm (7.6 g) and b.p. 185–205°/0.1 mm (7.4 g) were obtained. The residue (18.3 g) was a dark brown resin. The first fraction was acetylated and the acetate subjected to chromatography. Elution with light petroleum gave a crude crystalline acetate, m.p. 50–60° (5.2 g). Acetylation of the second fraction and seeding with crystals from the first one gave a further amount (2.8 g) of the acetate. Recrystallisation from methanol furnished the acetate as colourless rods, m.p. 92–93°,  $[\alpha]_D^{20} -9 \pm 1^\circ$  ( $c = 1.5$ ; ethanol). (Found: C 80.6; H 9.7; O 9.9; mol.wt. (Rast) 329.  $C_{28}H_{48}O_2$  requires C 80.4; H 9.8; O 9.7; mol.wt. 328.5).  $\lambda_{max}$  (in ethanol) 268  $m\mu$  ( $\log \epsilon$  3.71).

Hydrolysis with N potassium hydroxide and chromatography in light petroleum-ether mixture gave the free phenol as a semisolid mass,  $[\alpha]_D^{25} +43 \pm 1^\circ$  ( $c = 1.5$ ; ethanol),  $\lambda_{max}$  (in ethanol) 282  $m\mu$  ( $\log \epsilon$  3.70). From this a small amount of crystals with m.p. 56–57° could be obtained.

The benzoate was obtained from the acetate (100 mg) by hydrolysis followed by benzylation with benzoyl chloride in pyridine. After chromatography, crystallisation from methanol and sublimation it had m.p. 154.5–156° (yield 20 mg).

*$\beta$ -Sitosterol.* Recrystallisation of the sterol from alcohol gave leaflets of m.p. 139–139.5°,  $[\alpha]_D^{20} -35.5 \pm 1^\circ$  ( $c = 1.0$ ; chloroform). The acetate had m.p. 126–127°,  $[\alpha]_D^{20} -41.3 \pm 1^\circ$  ( $c = 1.0$ ; chloroform), the benzoate m.p. 148–149°,  $[\alpha]_D^{20} -13.0 \pm 1^\circ$  ( $c = 1.0$ ; chloroform) and the 3,5-dinitrobenzoate m.p. 203.5–205°,  $[\alpha]_D^{20} -12.5 \pm 0.5^\circ$  ( $c = 1.0$ ; chloroform). All these values correspond well with those given for  $\beta$ -sitosterol<sup>7</sup>.

*Xanthoperol.* Recrystallisation from benzene gave xanthoperol as yellow needles. It decomposes between 255 and 270°,  $[\alpha]_D^{20} +132.5 \pm 2.5^\circ$  ( $c = 1.2$ ; ethanol). (Found: C 76.1; H 8.4; O 15.5; mol.wt. (Rast) 303.  $C_{30}H_{48}O_2$  requires C 76.4; H 8.3; O 15.3; mol.wt. 314). IR-maxima: (KBr) 3 380 (s), 2 960 (m), 2 910 (m), 2 870 (m), 1 717 (m), 1 658 (s), 1 595 (s), 1 567 (s), 1 508 (m), 1 470 (m), 1 365 (w), 1 327 (s), 1 290 (s), 1 261 (s), 1 180 (m), 1 163 (m), 1 149 (m), 1 108 (w), 1 047 (w), 917 (w), 883 (w)  $cm^{-1}$ .

Xanthoperol is soluble in alkali and conc. sulphuric acid with a strong yellow colour. It gives no colouration either with ferric chloride, or with diazotised benzidine.

*Xanthoperol acetate.* Xanthoperol (20 mg) mixed with acetic anhydride (1 ml), and pyridine (3 drops) was allowed to stand for 3 days at room temperature. The mixture was poured into water and the precipitate recrystallised from dilute ethanol giving yellow rods (13.5 mg), m.p. 157.5–158.5°. (Found: C 74.0; H 7.95.  $C_{28}H_{48}O_4$  requires C 74.1; H 7.9).

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#### REFERENCES

1. Bredenberg, J. B. and Gripenberg, J. *Acta Chem. Scand.* **8** (1954) 1728.
2. Erdtman, H. in Cook, J. W. (editor) *Progress in Organic Chemistry* **1** (1952) 22.
3. Morton, R. A. and Stubbs, A. L. *J. Chem. Soc.* **1940** 1347.
4. Lemon, H. W. *J. Am. Chem. Soc.* **69** (1947) 2998.
5. Parham, W. E., Wheeler, E. L. and Dodson, R. M. *J. Am. Chem. Soc.* **77** (1955) 1166.
6. Gates, M. *Private communication*.
7. *Elsevier's Encyclopedia of Organic Compounds Ser III Vol 14* (1940) 90.

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