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The Constitution of "Cryptopinone"

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In 1947 two of us [1] reported the isolation of a carbonyl compound, $C_{20}H_{30}O$, from the twig roots and resinified trunks of Scots fir (*Pinus sylvestris* L.). This compound was given the name "cryptopinone" and tentatively regarded as a ketone. Shortly afterwards Harris and Sanderson [2] described the isolation of a neutral compound, $C_{20}H_{30}O$, from commercial wood and gum rosins (from *P. palustris* and *P. caribaea*). A comparison of physical constants (see Table 1) led Harris and Sanderson to suggest that these two substances were identical.*

Table 1.

Compound	Sörensen and Bruun [1] and this paper	Harris and Sanderson [2]
Free aldehyde ("cryptopinone")	m. p. 50– 52°	m. p. 50– 52°
Semicarbazone	m. p. 223–224°	m. p. 223–225°
2,4-Dinitrophenylhydrazone	m. p. 195–196°	m. p. 192–194°

* Since this paper was submitted for publication Dr. G. C. Harris has kindly carried out a direct comparison of the 2,4-dinitrophenylhydrazones of his carbonyl compound and of "cryptopinone". Dr. Harris writes:

The melting point of the 2,4-dinitrophenylhydrazone of cryptopinone in our apparatus was found to be 195–196.5° C. The melting point of the corresponding derivative of isodextropimarinal is 192–194° C. A mixed melting point of the two showed no depression at 193–195° C. Further evidence of the identity of the two substances was their identical x-ray diffraction patterns.

On these bases it may be said that cryptopinone and isodextropimarinal are the same compound.

We are very greateful to Dr. Harris for confirming this identity.

Harris and Sanderson [2] concluded that their compound was *isodextro*-pimarinal on the basis of dehydrogenation evidence and because chromic acid oxidation under mild conditions furnished *isodextro*-pimaric acid [3], m.p. 158—161°. The identity of the latter was said to be established by mixed m.p. and by its X-ray diagram.

We have now converted *dextro*-pimaric acid to the known *dextro*-pimarinol [4] and oxidised the latter under mild conditions to *dextro*-pimarinal. This aldehyde was shown to be identical with "cryptopinone" by comparison of the corresponding 2,4-dinitrophenylhydrazones. The identity was established by crystal form, m.p., mixed m.p., optical rotation and absorption spectrum. We conclude, therefore, that "*cryptopinone*" *is, in fact, dextro-pimarinal.* This conclusion is in agreement with the evidence of Harris and Sanderson *except* so far as the oxidation to *isodextro*-pimaric acid is concerned. In an effort to explain the discrepancy authentic *isodextro*-pimaric acid was reduced by lithium aluminium hydride to *isodextro*-pimarinol and the latter oxidised under mild conditions to *isodextro*-pimarinal, characterised as the 2,4-dinitrophenylhydrazone. The latter was entirely different from "cryptopinone" (*dextro*-pimarinal) 2,4-dinitrophenylhydrazone. Furthermore it melted at 180—182° and did not correspond, therefore, to the 2,4-dinitrophenylhydrazone, m.p. 192—194°, obtained by Harris and Sanderson [2] from their naturally occurring carbonyl compound. We are forced to conclude that, in spite of the reported evidence to the contrary, the acid obtained by Harris and Sanderson by oxidation was really *dextro*-pimaric acid *not isodextro*-pimaric acid.

EXPERIMENTAL

M.ps. are uncorrected. Rotations were determined, unless stated to the contrary, in chloroform solution at room temperature, which varied from 15 to 20°. Values of $[\alpha]_D$ have been approximated to the nearest degree. Absorption spectra were taken in chloroform solution using a Unicam S. P. 500 Spectrophotometer.

"*Cryptopinone*" *semicarbazone.* The previously described preparation was recrystallised as long needles from warm (but not hot) ethyl acetate. It had m. p. 228—230° decomp. (taken using a paraffin bath, but 223—224° decomp. taken, as before, using a concentrated sulphuric acid bath), $[a]_D$ + 57° (c, 1.91).

"*Cryptopinone*" *2,4-dinitrophenylhydrazone.* "Cryptopinone" regenerated from the semicarbazone as reported previously [1], was treated with a methanolic hydrochloric acid solution of 2,4-dinitrophenylhydrazine in the usual way. The crystalline orange ppt. was filtered and purified by filtration through alumina in benzene followed by crystallisation from chloroform-methanol. "Cryptopinone" 2,4-dinitrophenylhydrazone crystallised in orange needles, m. p. 195—196° decomp., $[\alpha]_D$ — 26° (c, 2.09), λ max. 360 mμ, ε max 26,000 (Found: C, 67.0, 67.4; H, 6.9, 7.4; N, 12.2. $C_{26}H_{34}N_4O_4$ requires C, 66.95; H, 7.35; N, 12.0 %).

dextro-*Pimarinal 2,4-dinitrophenylhydrazone. dextro*-Pimarinol [4] (350 mg), prepared by lithium aluminium hydride reduction of a specimen of *dextro*-pimaric acid kindly supplied by the U. S. Dept. of Agriculture, was dissolved in 10 ml of "Analar" acetic acid and oxidised by the addition of 100 mg of chromium trioxide dissolved in a few drops of water. The homogeneous solution was left overnight at room temperature. Addition of water and working up in the usual way gave oily *dextro*-pimarinal. For characterisation this was converted to the 2,4-dinitrophenylhydrazone in the same way as for "cryptopinone". Filtration through alumina and recrystallisation from chloroform-methanol afforded fine orange needles of *dextro*-pimarinal 2,4-dinitrophenylhydrazone, m. p. 195—196° decomp., $[\alpha]_D$ — 27° (c, 3.15), λ max 360 mμ, ε max 27 800 (Found: C, 66.75; H, 7.3; N, 12.0. $C_{26}H_{34}N_4O_4$ requires C, 66.95; H, 7.35; N, 12.0 %). Admixture of this 2,4-dinitrophenylhydrazone with the corresponding derivative of cryptopinone (see above) gave a m. p. of 195—196° decomp. (all three m. ps. taken at the same time).

isodextro-*Pimarinal 2,4-dinitrophenylhydrazone. isodextro*-Pimaric acid, m. p. 155—157°, $[\alpha]_D$ + 0.6° (c, 9.59), — 2.5° (c, 7.68) in alcohol, (250 mg) was reduced with lithium aluminium hydride to *isodextro*-pimarinol and the latter oxidised with chromium trioxide as for *dextro*-pimarinol (see above). The oily *isodextro*-pimarinal was converted to the 2,4-dinitrophenylhydrazone in the usual way. Filtration in benzene solution through alumina and recrystallisation from chloroform-methanol furnished the yellow *isodextro*-pimarinal 2,4-dinitrophenylhydrazone, m. p. 180—182° decomp., $[\alpha]_D$ + 104° (c, 0.41), λ max 360 mμ, ε max 25 600. (Found: C, 67.3; H, 7.6; N, 12.2. $C_{26}H_{34}N_4O_4$ requires C, 66.95; H, 7.35; N, 12.0 %). There was a marked depression in m. p. on admixture with "cryptopinone" 2,4-dinitrophenylhydrazone (see above).

SUMMARY

"Cryptopinone" isolated from *Pinus sylvestris*. L., has been proved to be *dextro*-pimarinal by a partial synthesis of the latter from *dextro*-pimaric acid.

We thank Dr. G. C. Harris for a gift of *isodextro*-pimaric acid and Mr. C. J. W. Brooks for the preparation of the *dextro*-pimarinol.

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