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XYLOSPYRIN - A NOVEL TRINAPHTHYLENEQUINONE FROM DIOSPYROS CHLOROXYLON AND COMMENTS ON PMR SPECTRUM OF (-) ISODIOSPYRIN LEUCOHEXAACETATE

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We have earlier reported the isolation of the binaphthaquinones, diospyrin and (-) isodiospyrin from the wood of Diospyros chloroxylon[1]. We now report the isolation of a new trinaphthylenequinone from the same source and name it Xylospyrin. On chromatography of the crude chloroform extract of the wood on a silica gel column with chloroform-benzene (4:1), 7-methyljuglone elutes first. Other successive fractions contain diospyrin, diospyrin-isodiospyrin mixture and diospyrin-xylospyrin mixture. From the latter mixture, we were able to separate xylospyrin by chromatography over a silica gel column with chloroform; bright yellow crystals from chloroform not melting upto 400°C. Found C 70.50 H 3.94%; $C_{33}H_{18}O_9$ requires C 70.97 H 3.25%; mol. wt. 558 by mass spectrum.

Its alcoholic solution gives an immediate purple colour with dil. caustic soda and warming with boric acid and acetic anhydride gives a deep crimson colour indicative of a peri-hydroxyquinone system. A negative Craven's test on the trimethylether points to the absence of free vinylic protons. Methyl iodide and silver oxide give a trimethylether. Found C 71.78 H 4.50%; $C_{36}H_{24}O_9$ requires C 71.99 H 4.03%; not melting upto 400°C; mol. wt. 600 by mass spectrum. Since no absorption for -OH groups can be seen in the IR spectrum of the parent compound, all three hydroxyl groups must be in peri positions; this is further supported by two carbonyl peaks at 1665 cm^{-1} and 1630 cm^{-1} in xylospyrin, the trimethylether giving only one carbonyl absorption at 1660 cm^{-1}, (KBr). The u.v. spectra of xylospyrin, $\lambda_{max}^{dioxane}$ 228, 276, 299 and 421 (log ϵ 4.80, 4.54, 4.53 and 4.09) and its trimethylether $\lambda_{max}^{dioxane}$ 223, 273 and 391 (log ϵ 4.76, 4.57 and 4.01) resemble that of diospyrin[2] and isodiospyrin[1].

Because of solubility difficulties we could not record a PMR spectrum of xylospyrin, but this was possible for its trimethylether in $CDCl_3$* (Fig. 1). The apparent symmetry of the

* Chemical shifts in δ = ppm relative to TMS as external standard.

molecule is clear; there are two sharp singlets at 2.51 and 4.06 ppm assignable to the aromatic methyl and methoxyl groups respectively. There are only two more signals at 7.14 ppm and 7.61 ppm; these are broad (width at half height 2.5 cps) and can be assigned to metacoupled aromatic protons. There are no signals for vinylic protons. The relative intensity of the

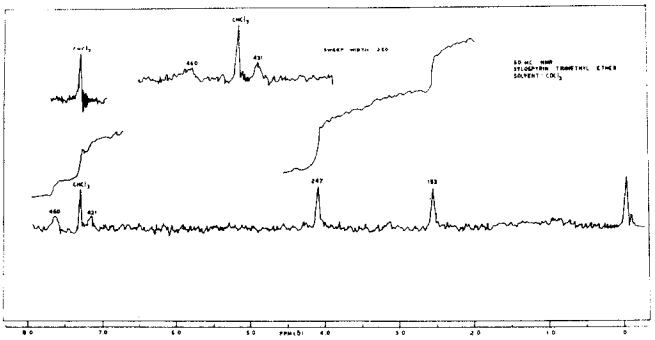


Fig. 1

four signals is in the ratio of 3:3:1:1. The difference of 42 units between the mol. wt. of xylospyrin and its methylether clearly shows the latter to have three methoxyl groups and thus there are three aromatic methyl groups, three methoxyl groups and six aromatic protons in the molecule.

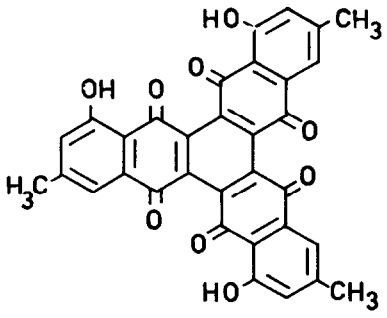
The different proton chemical shifts observed in the PMR spectrum of xylospyrin trimethylether compare well with the chemical shifts of the methyl, methoxyl and two aromatic protons of 7-methyljuglone methylether and the 5-methoxyl, 7-methyl and the 6 & 8-aromatic protons of diospyrin dimethylether. The proton chemical shifts of these compounds are listed in Table 1.

TABLE 1

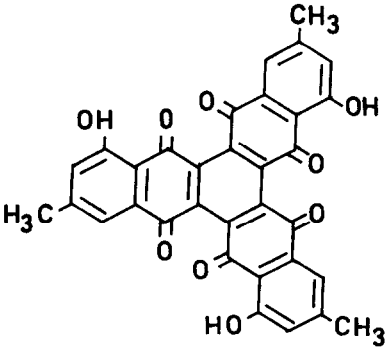
	CH_3	OCH_3	H	H
7-Methyljuglone methylether	2.48	3.98	7.10	7.55
Diospyrin dimethylether	2.50	4.03	7.16	7.61
Xylospyrin trimethylether	2.51	4.06	7.14	7.61

(Solvent $CDCl_3$)

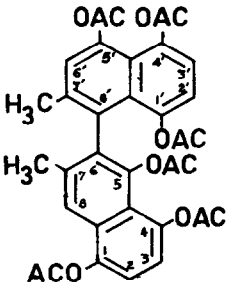
From the above evidence it is possible to visualise that xylospyrin originates by the condensation of three molecules of 7-methyljuglone with the loss of six vinylic protons. If this assumption is correct, only two alternate structures (I and II) can be written for xylospyrin.



I



II



III

These trinaphthylene structures draw some support from the fact that synthetic trinaphthylenequinones such as triphthaloylbenzene[3] are also yellow crystalline solids sparingly soluble in organic solvents and not melting upto 400°C.

The mass spectra of xylospyrin and its trimethylether consist of peaks of low intensity as both the compounds are difficult to volatilise. In general the essential features of the fragmentation of 7-methyljuglone and its methylether are preserved. The main fragmentation is through the loss of a series of carbon monoxide molecules and formyl radicals. Doubly charged ions (m/e 279 and 300 respectively) are prominent in both cases.

We were earlier not able to obtain isodiospyrin in a completely pure state. This has later been isolated by A.L. Fallas and R.H. Thomson[4] in a pure state from D. mespiliformis and D. virginiana. We have now been able to purify our (-) isodiospyrin. It has the same physical constants and PMR spectrum but the leucohexaacetate (III) prepared from our isodiospyrin (m.p. 134°; found C 64.01 H 4.55%; $C_{34}H_{30}O_{12}$ requires C 64.76 H 4.76%) gives a very much better resolved PMR spectrum (Fig. 2) than that described by A.L. Fallas and R.H. Thomson. In their spectrum five aromatic protons give one singlet at 7.10 ppm. In our spectrum this singlet integrates only for three protons, the other two protons giving two one proton doublets

at 7.06 and 7.26 ppm (J = 8 cps) assignable to the C-2 and C-3 orthocoupled protons (cf. similar protons in diospyrin leucohexaacetate)[2]. Also the one proton signal at 7.75 ppm is a quartet in

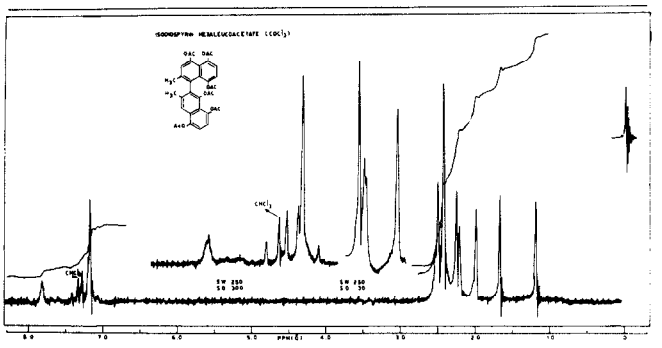


Fig. 2

our leucoacetate and not a singlet as in Fallas and Thomson's compound. It is assignable to the C-8 proton which shows allylic coupling with the C-7 methyl doublet at 2.19 ppm. The C-7' methyl should be assigned the 1.96 ppm signal. Fallas and Thomson's assignment of the six proton peak at 2.40 ppm to the two Ar-CH_3 groups is erroneous and does not take into account the ring-current shielding of these groups which are in ortho positions to the biphenyl linkage[1,2]. The other methyl signals at 1.16, 1.65, 2.24, 2.40 and 2.80 ppm are assignable to the -$OCOCH_3$ protons. The splitting of the C-7 methyl and the absence of this splitting in the C-7' methyl lend support to the localisation of the bonds in substituted naphthalenes and we will cite more instances in another publication.

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