(FG) from the partial hydrolysates. This was purified, compared with synthetic material and identified by similar procedures as for FGP.

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13-OXOMYRICANOL, A NEW [7.0]-METACYCLOPHANE FROM *MYRICA NAGI*

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(*Revised received* 12 *September* 1979)

Key Word Index—*Myrica nagi*; Myricaceae; diarylheptanoid; [7.0]-metacyclophane; 13-oxomyricanol.

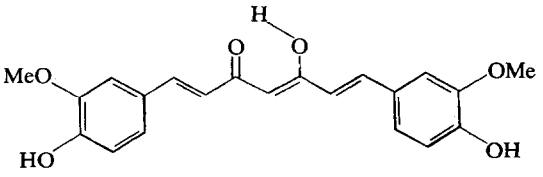
Abstract—A new [7.0]-metacyclophane has been isolated from the root bark of *Myrica nagi*. On the basis of spectroscopy the constitution of the new compound is proposed to be 13-oxomyricanol.

INTRODUCTION

Diarylheptanoids comprise a class of natural products based on 1,7-diphenylheptane. They are rare, but *ca* 40 substances are known from one family in the monocotyledons (Zingiberaceae) and four in the dicotyledons, of which the Betulaceae and the Myricaceae are richest in these substances. Most diarylheptanoids are acyclic, with curcumin (**1**), the pigment of *Curcuma longa* rhizomes [1], as an example.

Some diarylheptanoids with a skeletal structure based on diphenyl ([7.0]-metacyclophanes) or diphenyl oxide (14-oxa-[7.1]-metaparacyclophanes) are known. Both types are constituents in the genus *Myrica*: myricanol (**2**) and myricanone (**3**), isolated from *M. nagi* [2], and porson (**4**) from *M. gale* [3] are examples of the diphenyl type, while galeon (**5**) and hydroxygaleon (**6**), both from *M. gale* [4], are of the diphenyl oxide type.

In this communication we wish to report the isolation of a new [7.0]-metacyclophane from *Myrica nagi*. Its constitution was established as 13-oxomyricanol (**7**) on the basis of spectroscopic evidence.



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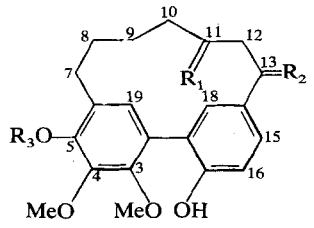
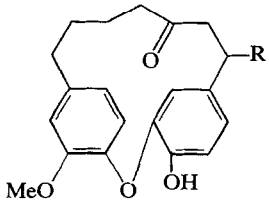


2 R_1 = H, OH; R_2 = H, H; R_3 = H

3 R_1 = O; R_2 = H, H; R_3 = H

4 R_1 = O; R_2 = H, OH; R_3 = Me_3

7 R_1 = H, OH; R_2 = O; R_3 = H



5 R = H
6 R = OH

RESULTS AND DISCUSSION

The new substance was isolated from an extract of root bark of *M. nagi*, generously given to us by Professor Lawrence Crombie, University of Nottingham. Purification of the crude extract by preparative TLC yielded, along with **2** and **3**, a small amount (*ca* 7% of the total extract) of another, more polar UV-absorbing substance. This substance was purified by repeated TLC and finally by recrystallization from aqueous MeOH, mp 240°, $[\alpha]_D^{20} - 36°$. According to high resolution MS, its molecular formula was established as $C_{21}H_{24}O_6$. The UV spectrum, with absorptions at 281, 263 and 224 nm, resembles the spectra of known [7.0]-metacyclophanes [2, 3]. In the IR spectrum an absorption maximum at 1664 cm^{-1} indicated a conjugated ketone.

The ^1H NMR spectrum was in many respects reminiscent of the spectra of other [7.0]-metacyclophanes from *Myrica* [2, 3]. The 5 side-chain methylene groups form overlapping multiplets in the region 1.4–3.8 ppm, while the methine proton H-11 is clearly visible as a one-proton multiplet at 4.14 ppm. Three one-proton singlets at 3.49, 6.0 and 8.48 ppm which disappear on shaking with D_2O, were ascribed to the hydroxy groups located at C-11, C-5 and C-17, respectively. The corresponding hydroxy signals in the ^1H NMR spectrum of myricanol are found in the same region of the spectrum [2]. The aromatic protons H-16, H-15 and H-18 form an AMX pattern at 7.04, 7.89 and 8.07 ppm, respectively, while H-19 is a singlet at 6.94 ppm. Protons H-15 and H-18 are shifted by *ca* 0.9 ppm down-field compared to the corresponding protons in myricanol, while H-16 and H-19 are only slightly shifted. This strongly indicates that the carbonyl group is located at C-13, a fact which is supported by the typical aryl-conjugated carbonyl stretching frequency (1664 cm^{-1}). In the ^{13}C NMR spectrum, the aliphatic region was very similar to the myricanol spectrum [5]. Tentative assignments are given in Table 1. The main differences in the spectra were firstly that the myricanol resonance at 34.5 ppm, assigned to C-13, was not present due to the introduction of a carbonyl group in this position, secondly that this had caused the neighbouring C-12 to resonate 22.1 ppm further down-field. In the aromatic region both C-15 and C-17 were further down-field, 7.2 and 6.9 ppm, respectively. The shift difference for C-17 agrees well with predicted values [6], but the shift for C-15 was somewhat unexpected. It may be due to the fact that the carbonyl function, in this molecule, is fixed *syn* relative to C-15. A corresponding down-field shift was not observed for the other *ortho*-carbon, C^{-18}, which is *anti*. The ^{13}C resonances from the aryl ring farthest away from C-13 seem to undergo only small shift changes on going from myricanol to 13-oxomyricanol, as do the resonances from C-7 to C-10 and the methoxy carbons. In addition, the C-11 to C-13 disubstitution pattern was previously known in porson [3] and hydroxygaleon [4], while C-7 oxygenated [7.0]-metacyclophanes seem to be unknown as plant constituents.

The MS shows the M^+ as base peak with most of the other peaks at less than 10% relative intensity. This is in accordance with earlier studies on other [7.0]-metacyclophanes [2, 3]. Most of the fragments can be assigned to fragmentations in the side-chain: *m/e* 343 ($M^+ - CHO$), 329 ($M^+ - C_3H_7$), 301 ($M^+ - C_4H_7O$), 287 ($M^+ - C_5H_9O$), 271 ($M^+ - C_5H_9O_2$), 259 and 258 ($M^+ - C_6H_9O_2/C_6H_{10}O_2$) and 105 ($C_6H_{11}O_2$). Corresponding cleavages have been observed earlier in other *Myrica* cyclophanes [2–4].

The spectral evidence thus seems to point to 13-oxomyricanol, (systematic name: 5,11,17-trihydroxy-3,4-dimethoxy-13-oxo-[7.0]-metacyclophane) as the structure for the new compound. This compound seems to be related to the known [7.0]-metacyclophanes of *M. nagi*, having a 5,17-dihydroxy-

Table 1. Assignment of signals in the ^{13}C NMR spectra of myricanol and 13-oxomyricanol

δ values		
Myricanol	13-Oxomyricanol	Position
22.8	22.7	C-8, C-9, C-10
25.4	25.3	
25.6	25.3	
26.8	48.9	C-12
34.5	not recorded	C-13
39.3	38.1	C-7
61.3	61.3	2×OMe
61.3	61.3	
68.3	71.0	C-11
116.5	118.0	C-16
122.5	123.0	C-6
123.1	121.7	C-1, C-2
124.4	124.1	
129.1	128.4	C-18, C-19
129.6	128.5	
130.5	not recorded	C-14
132.8	140.0	C-15
138.4	not recorded	C-3, C-4
145.6	not recorded	
147.5	148.3	C-5
150.9	157.8	C-17

3,4-dimethoxy substitution pattern in the aromatic part of the molecule, and also to the 11,13-dioxygenated cyclophanes of *M. gale*. Further studies on the stereochemistry and spectroscopy of these unusual substances are in progress.

EXPERIMENTAL

Mps are uncorr. and optical rotations were measured in 10 cm cells.

A crude myricanol extract from *M. nagi* [2] (275 mg) was purified by prep-TLC (Merck Fertigplatten GF_{254} 0.2 mm, eluent C_6M_6–Me_2CO, 19:1). This extract yielded myricanone (**3**), R_f 0.8, 35 mg, and myricanol (**2**), R_f 0.55, 207 mg, both with R_f values and spectral data in accordance with authentic samples. In addition, another more polar substance (**7**) R_f 0.3, 19 mg, was isolated. This substance was further purified by repeated TLC and crystallization from MeOH–H_2O (4:1), yielding colourless microcrystals, mp 239.5–240°, $[\alpha]_D^{20}$ −36° (*c* 0.31, $CHCl_3$), $[\alpha]_{546}^{20}$ −51°, $[\alpha]_{436}^{20}$ −225°, $[\alpha]_{365}^{20}$ *ca* −1100°. UV λ_{max}^{MeOH} nm (log ε): 281 *sh* (4.01), 262 (4.24), 224 (4.23). IR ν cm^{-1}: KBr 3350, 2930, 2860, 1664 (*s*), 1612, 1573 (*s*), 1495, 1453 (*s*), 1409 (*s*), 1348 (*s*), 1226 (*s*), 1167, 1103, 1060, 1048, 1005, 973, 930, 918, 894, 829. ^1H NMR (100 MHz, $CDCl_3$): δ 1.4–3.8 (several overlapping *m*, 10H), 3.49 (1H, *s*, disapp. with D_2O), 3.92 (3H, *s*), 4.01 (3H, *s*), 4.14 (1H, *m*), 6.0 (1H, *br s*, disapp. with D_2O), 6.94 (1H, *s*), 7.04 (1H, *d*, $J = 8$ Hz), 7.89 (1H, *dd*, $J = 2$ and 8 Hz), 8.07 (1H, *d*, $J = 2$ Hz), 8.48 (1H, *s*, disapp. with D_2O). ^{13}C NMR (25.1 MHz, $CDCl_3$): δ 22.7, 25.3 (2 peaks), 38.1, 48.9, 61.3 (2 peaks), 71.0, 118.0, 121.7, 123.0, 124.1, 128.4, 128.5, 140.0, 148.3, 157.8. MS (IP 70 eV, *m/e* (%)): 372 (100, M^+), 355 (8, M^+-17), 343 (7, M^+-29), 329 (13, M^+-43), 323 (4, M^+-49), 301 (6, M^+-71), 287 (4, M^+-85), 271 (4, M^+-101), 259 (8, M^+-113), 258 (8, M^+-114), 143 (13), 115 (5). No metastable peaks were observed. M^+ obs. 372.1573 as calc. for $C_{21}H_{24}O_6$.

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THREE NEW FLAVONOIDS FROM *TEPHROSIA PRAECANS*

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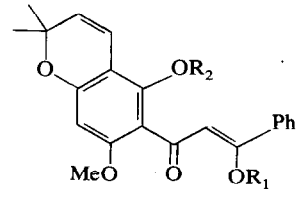
Key Word Index—*Tephrosia praecans*; Leguminosae; β-hydroxy- and β-methoxychalcones; chromenoflavone; chromenoflavanone.

In continuation of our study on the flavonoids and rotenoids of Leguminosae [1], we examined *Tephrosia praecans*. The oily residue obtained from $CHCl_3$ extraction of the seeds gave by chromatography on Si gel four pure compounds together with a mixture of tephrosin and 12a-hydroxyrotenone.

The main component, $C_{23}H_{24}O_5$ (M^+ at *m/e* 380), named praecansone A, showed λ_{max} at 284 nm and ν_{max} at 1660 cm^{-1}. The ^1H NMR spectrum gave evidence of a dimethylchromene ring, three methoxyl groups, two aromatic/olefinic protons and a C_6H_6 conjugated to a double bond. From the above data structure **1** can be assigned to praecansone A and the mass fragmentation is in agreement. Further confirmation



	R_1	R_2
1	Me	Me
2	H	Me
6	H	H