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Identification and determination of the main constituents of phenol tar with carbon- and proton-NMR spectroscopy

Maciej Skarżyński,*[a] Edyta Wielogórska[b] and Hanna Otwinowska[a]

[a] *Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*
[b] *Department of Chemistry, University of Warsaw, Warsaw, Poland*

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^{13}C and ^{1}H NMR were employed for the identification and determination of the main constituents of phenol tar from the phenol industrial synthesis process. The carbon and the proton spectra were correlated with each other with a 2D-HETCOR experiment. The presence of cumyl phenyl ether, not previously reported, was found and confirmed by the mass spectrum. ^{1}H NMR determinations of six compounds were repeated at 100 and 500 MHz and no significant difference in the repeatability and the accuracy between the results was found.

Phenol tar is a by-product stream of the cumene-to-phenol process and consists of compounds formed at two stages of the process: oxidation of cumene to cumene hydroperoxide (CHPO) and cleavage of CHPO to phenol and acetone. Qualitative and quantitative analysis of phenol tars (or pitches) employing chromatographic techniques has been the subject of numerous studies.[1–4] Infrared spectroscopy was applied to the determination of their main components by Górska and Gluzińska.[5] Quantitative analysis of samples of phenol tars and other streams from the process with proton NMR spectroscopy was carried out by Skarżyński *et al*.[6] Carbon NMR was applied by Malik *et al.*[7] for the identification of the main components of dimeric fractions from the distillation of tars. Analysis of the proton and carbon NMR spectra of isomeric cumylphenols was the subject of a study by Skarżyński and Jakubowski.[8]

The most important analysis of phenol tar, connected with the mass balance of the process, is the determination of phenol. This can be done more or less exactly by numerous methods, including ^{13}C NMR, as shown in our previous study.[9] The purpose of this work was to show that ^{13}C NMR along with ^{1}H NMR spectroscopy may be used for the identification and simultaneous determination of the other main constituents of the tar. The analysis employs signals from the aliphatic region of the spectra, much more transparent and much easier for making assignments than the aromatic region (this is not possible in the case of phenol). The three phenol tar samples analysed in two studies, denoted tar 1, tar 2 and tar 3, were taken at random directly from the process at the Petrochemia plants, Płock, Poland. The samples differed greatly in their quantitative composition, mainly in the content of phenol, which varied from below 3% in tars 1 and 2 to over 40% in tar 3.

Experimental and results

The 100 MHz ^{1}H NMR and 25 MHz INVGATE ^{13}C NMR spectra were obtained with a Bruker (Rheinstetten, Karlsruhe, Germany) WP-100SY spectrometer and 500 MHz ^{1}H NMR spectra were obtained with a Varian (Palo Alto, CA, USA) UNITY PLUS-500 spectrometer. Pulses of 60° (π/3) at intervals of 10.0 s were applied for acquisition of the proton spectra, while the carbon spectra were acquired by using 90° (π/2) pulses at intervals of either 17.5 s (tars 1 and 2, *cf.* ref. 9) or 26.0 s (tar 3). The time domain (TD) was 32K data points for both the proton and carbon spectra; ^{1}H free induction decay (FID) curves were transformed at 32K, while ^{13}C FIDs were exponentially multiplied (line broadening factor LB = 0–0.5 Hz) and transformed at either 32K or 64K. All measurements were carried out at room temperature. The tar samples were analysed either undiluted with a drop of deuterated cyclohexane as a lock (^{13}C NMR), or dissolved at a concentration of about 10% in deuterated chloroform (^{1}H NMR). Tetramethylsilane (TMS) was added to each sample as an internal chemical shift standard. All samples were sealed in tubes of 5 mm diameter to prevent changes in composition between subsequent analyses and during accumulation of spectra.

Longitudinal relaxation times T_{1C} (25 MHz) were measured at 25 °C with the inversion–recovery pulse sequence, with proton-decoupling frequency on during the π/2 pulse and the FID acquisition only. ^{13}C NMR subspectra were edited by combining the DEPT (distortionless enhancement by polarization transfer) and GASPE (gated spin echo) techniques. Heteronuclear carbon–proton correlation spectrum ($F2$ ^{13}C 125 MHz, $F1$ ^{1}H 500 MHz) was obtained with the two-dimensional spin echo technique.

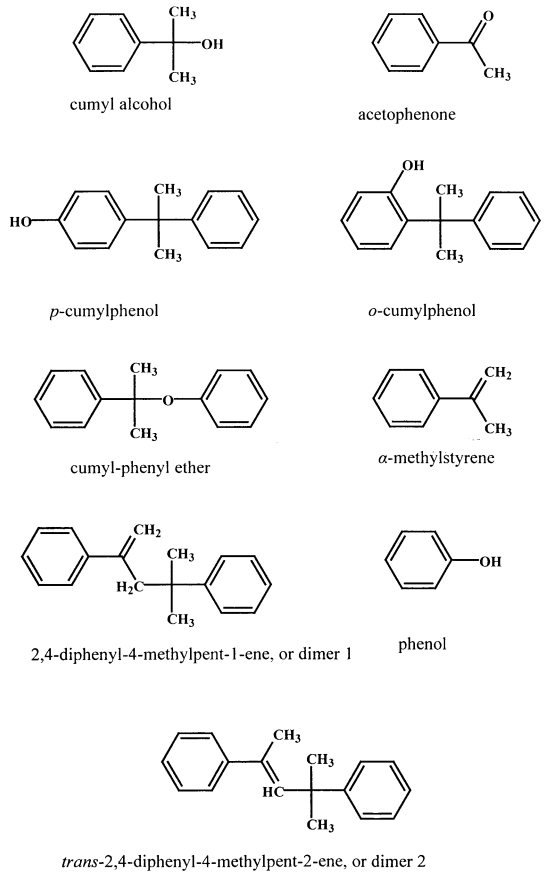
1,4-Dioxane (analytical-reagent grade) to be used as the standard for quantitation of the NMR results was rectified and the 100.99–101.04 °C fraction was retained and kept over 4 Å molecular sieves (its chemical shifts are δ_C = 67.1 ppm and δ_H = 3.70 ppm). Quantitative results were obtained by approximating field areas of signals by the field areas of triangles (or by the products of their heights and half-widths), as described in ref. 9.

Qualitative analysis

The main components of the phenol tar, the presence of which has been reported in the chromatographic and spectroscopic studies mentioned above,[1–7] are cumyl alcohol, acetophenone, *p*- and *o*-cumylphenols, α-methylstyrene and two of its dimers (2,4-diphenyl-4-methylpent-1-ene and *trans*-2,4-diphenyl-4-methylpent-2-ene, denoted as dimer 1 and dimer 2, respectively) and phenol. However, any technological modifications to the process may cause changes in the quantitative and qualitative composition of its streams and new compounds can be formed. When the mode of adding sulfuric acid as a CHPO cleavage catalyst was changed from acetone-dissolved to undiluted, new signals in the NMR spectra of the tars appeared. In the aliphatic regions of the spectra these were (1) a ^{1}H-NMR signal at δ 1.69 ppm, in the group of signals of methyl group protons, shifted downfield from the signals of *p*- and *o*-cumylphenol by 0.09 and 0.03 ppm, respectively; and (2) two

signals in the ^{13}C NMR spectra, one at δ 29.9 ppm, assigned [DEPT, see Fig. 3(a)] to a CH_3 group, and the other at δ 80.0 ppm, assigned [GASPE, Fig. 3(d)] to a quaternary (unprotonated) carbon atom.

Analysis of a series of tars by NMR and GC–MS allowed one peak of an unknown compound to be selected in all chromatograms and assigned to cumyl phenyl ether ($C_{15}H_{16}O$, an



isomeric molecule to cumylphenols). The mass spectrum of the compound is shown in Fig. 1. The molecular peak appears at *m*/*z* = 212 and the main fragment (peak at *m*/*z* 119) is the cation produced by loss of a PhO group; the next step of fragmentation is typical for alkylbenzenes. The molecule of cumyl phenyl ether may be formed from molecules of phenol and cumyl alcohol with elimination of water (dehydration), so its formation must be favoured by any local acid condensations, which are in turn formed as the effect of adding undiluted acid.

Individual contents of all these compounds may vary over a wide range, but their sum is usually between 85 and 95%. There are also a few unidentified low molecular weight (probably dimeric) compounds in amounts of the order of 1%, manifesting

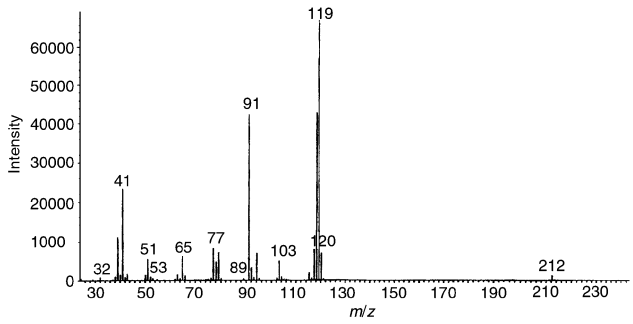


Fig. 1 Mass spectrum of cumyl phenyl ether. Molecular peak at *m*/*z* 212, peak of the base fragment at *m*/*z* 119.

themselves both in the chromatograms and the ^{13}C NMR spectra.

In addition, a large number of high molecular weight substances in small amounts are always present in the tar, from trimers to agglomerates with molecular weights of several thousands, identified neither in NMR nor IR spectra, and of which hardly any occur in the gas chromatograms, commonly used in industrial analysis. Gel permeation chromatography (GPC) was applied to estimate the percentages of fractions of molecules heavier than dimers in tars 1–3. Trimers (of molecular weight between 300 and 400) constituted 3–4% in tars 1 and 2 and 1% in tar 3. About 1.5% of tars 1 and 2 and about 0.5% of tar 3 consist of tetramers. Molecules heavier than tetramers (with molecular weights >500) constitute 1.5% of tars 1 and 2 (with 2×10^{-3}% of polymeric substances with molecular weights from 1500 to >4000) and 0.7% of tar 3. All these components constitute about 6–7% of tars 1 and 2 and >2% of tar 3. However, phenol tar samples were analysed with their total contents close to 20%.[10]

The two-dimensional heteronuclear ^{13}C–^{1}H NMR correlation spectrum (aliphatic part) of tar 1 is shown in Fig. 2. Edited ^{13}C-NMR subspectra are shown in Fig. 3. Chemical shift values of the signals observed in the ^{13}C and ^{1}H NMR spectra of the tars, δ_C and δ_H, and their assignments are compiled in Table 1.

Quantitative analysis

The fundamental problem of quantitative analysis by NMR spectroscopy (more ^{13}C NMR than ^{1}H NMR) is associated with longitudinal relaxation processes. Because of the slow relaxation (or long T_1 times), for the accumulation of a quantitative ^{13}C NMR spectrum, the use of either a long pulse repetition delay or a relaxing agent [*e.g.*, chromium *tris*(acetylacetonate)] is necessary. The presence of paramagnetic oxygen molecules dissolved in an analyte mixture also makes relaxation processes faster and the T_1 times shorter. Since the phenol tar is a product of vacuum distillation, one should expect it to be de-gassed and oxygen free, and very long relaxation times might be expected. However, the measurements of T_{1C} in the tar samples showed them to be relatively short (Table 1).

The most slowly relaxing aliphatic ^{13}C nuclei are those in the quaternary carbon atoms of cumylphenols, cumyl alcohol and dimer 1 (T_1 from 4.6 to 15.4 s), so their signals were excluded from the analysis. Comparatively long T_{1C} times, equal to 5.2 s

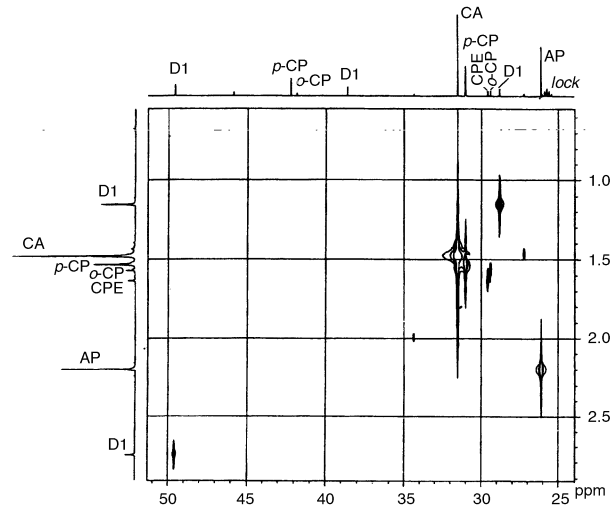


Fig. 2 The range of saturated aliphatic structures of the 2D-HETCOR ^{13}C-^{1}H NMR spectrum of tar 1 (^{13}C 125 MHz, ^{1}H 500 MHz). AP = acetophenone; CA = cumyl alcohol; *o*-CP = *o*-cumylphenol; *p*-CP = *p*-cumylphenol; CPE = cumyl phenyl ether; D1 = dimer 1.

in tar 3 and 3.0 s in tars 1 and 2, were measured in the methyl group of acetophenone and they are decisive as regards the pulse repetition delay (five times the longest T_1) that has to be applied to obtain spectra with quantitative relations between all the determined compounds. The other T_{1C} values are < 1 s.

The interval of 10 s between 60° pulses, applied for the accumulation of ^{1}H NMR spectra, is due to the relatively long (10 s) acquisition time of FIDs acquired at 100 MHz at 32K data points. Under these conditions, verified to be 'safe', quantitative relations were maintained between the areas of all signals in the proton spectra of tars.

The results of the NMR analyses are presented and compared with the average results of GC determinations in Table 2. Their consistency can be recognized as good with respect to typical results obtained in industrial analysis, and particularly consistent are the NMR results (*i.e.*, ^{1}H NMR at 100 and at 500 MHz and ^{13}C NMR). Their agreement with the GC results is significantly worse, while the average relative error of GC determinations of the main constituents in tar samples has been roughly estimated at 5–10%.[11] There is no evidence for less valuable proton NMR results being obtained at 100 MHz in comparison with those obtained at 500 MHz. Overlapping of the

Table 1 Chemical shifts δ_C and δ_H of signals in the ^{13}C and ^{1}H NMR spectra of phenol tars, and longitudinal relaxation times of ^{13}C nuclei T_{1C} in the analysed tar samples

				T_{1C}/s	
δ_C (ppm)[a]	δ_H (ppm)[b]	Compound	Structure	Tars 1 and 2[c]	Tar 3
26.1	2.49	Acetophenone	CH_3	3.0	5.2
27.0	1.48	CH_3 groups not assigned			
28.8	1.20	Dimer 1	$2CH_3$	0.5	0.7
29.4	1.63	*o*-Cumylphenol	$2CH_3$	0.9	
29.6	1.67	Cumyl phenyl ether	$2CH_3$	0.5	
31.0	1.59	*p*-Cumylphenol	$2CH_3$	0.3	0.5
31.5	1.54	Cumyl alcohol	$2CH_3$	0.6	0.9
34.4	2.10	CH_2 groups not assigned			
38.6	—	Dimer 1	C	7.4	9.1
41.9	—	*o*-Cumylphenol	C	4.6	15.4
42.3	—	*p*-Cumylphenol	C	6.1	9.9
45.9	—	Quaternary C atoms not assigned			
49.6	2.80	Dimer 1	CH_2	0.5	0.6
73.1	—	Cumyl alcohol	C	5.1	10.9
80.0	—	Cumyl phenyl ether	C	11.0	

[a] ^{13}C chemical shifts δ_C observed in undissolved tar samples. [b] ^{1}H chemical shifts δ_H observed in *ca.* 10% solutions of tars in deuterochloroform. [c] Differences between the T_{1C} values measured for particular structures in tars 1 and 2 varied from 0.0 to 0.4 s and in most cases did not exceed the error of a measurement; each result in the table is the higher one of the two; lack of a result means that the measurement was not possible because of small amount of a compound in the tar.

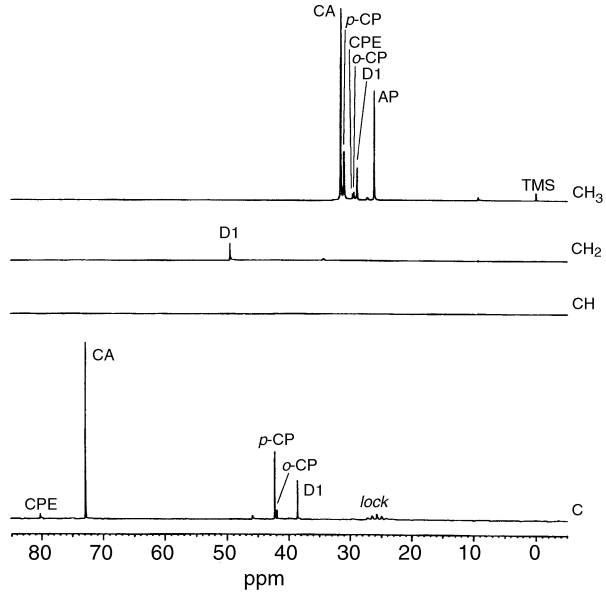


Fig. 3 Edited ^{13}C NMR subspectra (DEPT and GASPE) of tar 1. AP = acetophenone, CA = cumyl alcohol; *o*-CP = *o*-cumylphenol; *p*-CP = *p*-cumylphenol, CPE = cumyl phenyl ether; D1 = dimer 1.

Table 2 Comparison of the results of the determination of the six main components in three phenol tar samples by ^{1}H NMR (at 100 and 500 MHz), ^{13}C NMR (at 25 MHz) and gas chromatography

		Result of the determination (%)											
		^{1}H NMR (100 MHz)			^{1}H NMR (500 MHz)			^{1}H NMR	^{13}C NMR			NMR	
Tar No.	Component	1	2	Av.	1	2	Av.	(av.)	1	2	Av.	av.	GC
1	Cumyl alcohol	23.5	23.2	23.3	22.6	23.6	23.1	23.2	23.6	23.4	23.5	23.3	24.4
	Acetophenone	17.7	18.0	17.9	17.7	17.5	17.6	17.8	18.0	18.6	18.3	17.9	21.5
	p-Cumylphenol	14.1	13.9	14.0	13.7	13.6	13.7	13.8	14.0	14.2	14.1	13.9	13.1
	Dimer 1	10.0	10.2	10.1	9.3	9.1	9.2	9.7	10.4	10.6	10.5	9.9	10.2
	o-Cumylphenol	2.7	2.6	2.6	2.7	2.6	2.7	2.7	2.2	2.2	2.2	2.5	4.8
	Cumyl phenyl ether	2.3	2.4	2.4	2.4	2.5	2.4	2.4	2.6	2.8	2.7	2.5	nd[a]
	Sum			70.2			68.7	69.6			71.3	70.0	74.0
2	Cumyl alcohol	22.3	23.2	22.8	20.5	21.0	20.8	21.8	23.2	24.2	23.7	22.4	25.1
	Acetophenone	22.6	22.3	22.4	23.6	23.0	23.3	22.9	22.7	23.0	21.9	22.9	21.5
	p-Cumylphenol	14.4	14.4	14.4	13.5	13.7	13.6	14.0	15.6	15.4	15.5	14.5	15.7
	Dimer 1	12.0	12.2	12.1	11.1	12.0	11.5	11.8	12.2	11.7	12.0	11.9	13.9
	o-Cumylphenol	3.5	2.9	3.2	3.2	3.1	3.1	3.2	3.2	3.0	3.1	3.2	4.4
	Cumyl phenyl ether	1.9	1.3	1.6	1.7	1.6	1.7	1.6	2.0	1.6	1.8	1.7	nd
	Sum			76.5			74.0	75.3			78.0	76.6	80.6
3[b]	Cumyl alcohol	13.1	13.4	13.2	12.6	12.8	12.7	12.9	13.1	13.6	13.3	13.1	12.8
	Acetophenone	12.1	12.3	12.2	12.4	12.2	12.3	12.3	12.5	12.1	12.3	12.3	13.8
	p-Cumylphenol	6.7	6.6	6.6	6.5	6.8	6.6	6.6	6.7	6.8	6.7	6.7	4.4
	Dimer 1	4.7	4.2	4.5	4.6	4.3	4.5	4.5	4.7	4.7	4.7	4.5	4.0
	o-Cumylphenol	1.4	1.3	1.4	1.2	1.5	1.3	1.3	(+)[c]	(+)	(+)	1.4	1.2
	Cumyl phenyl ether	1.0	1.0	1.0	1.1	1.2	1.2	1.1	(+)	(+)	(+)	1.1	nd
	Sum			38.9			38.6	38.7			37.0	39.1	36.2

[a] nd = Not determined. [b] The main constituent is phenol; *cf.* ref. 9. [c] The (+) signs mean that the presence of the compound was stated and found below the limit of determinability (assuming an acceptable time of analysis at a ^{13}C frequency of 25 MHz).

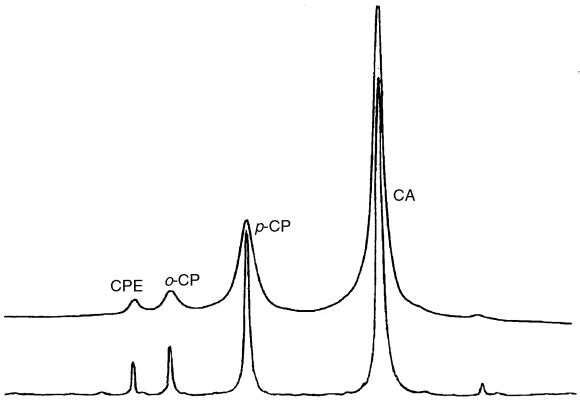


Fig. 4 Proton-NMR spectrum of tar 1 (δ range from 1.75 to 1.45 ppm) at 100 MHz (upper trace) and 500 MHz (lower trace). CA = cumyl alcohol;, *o*-CP = *o*-cumylphenol; *p*-CP = *p*-cumylphenol; CPE = cumyl phenyl ether.

proton signals at 100 MHz (see Fig. 4) would result in proportional overestimation of the content of a less abundant constituent, the signal of which overlaps with a more abundant constituent, *e.g.*, of *p*-cumylphenol at the expense of cumyl alcohol or *o*-cumylphenol at the expense of *p*-cumylphenol. No such effect was observed (although numerous cycles of analyses were repeated), so it may be assumed that the effect of overlapping of proton signals at 100 MHz is completely eliminated (within the limits of the accuracy of the method) by the applied procedure of comparing the triangular areas instead of the heights of the integral curves.

It should be finally concluded that there is at least one reason why quantitative NMR results can often be regarded as more accurate and more reliable than those obtained by any other method, namely the possibility of 'autocontrol' of the method, or verification of NMR results with further NMR results obtained with the same apparatus. Not only is it possible to make independent calculations of the same determination by using different signals of the same proton or carbon spectrum (an example of such a procedure for the determination of phenol by ^{13}C NMR has been described[9]), but also resonance spectra taken for different nuclei (*e.g.*, ^{1}H and ^{13}C, as described above) can be applied for independent determinations. This is particularly of great value in analysing multi-component complex mixtures such as industrial process streams.

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References

1 A. Švob, Đj. Deur-Šiftar and V. Jaun, *J. Chromatogr.*, 1968, **38**, 326.
2 K. Füllbier, W. Kiessling and K. K. Moll, *J. Prakt. Chem.*, 1970, **312**, 397 (in German).
3 H. Malikowska, H. Otwinowska, K. Gorczyńska, H. Waleędziak and A. Szostak, *Chem. Anal. (Warsaw)*, 1974, **19**, 511 (in Polish); *Chem. Abstr.*, 1975, **82**, 10 874v.
4 M. Šingliar, V. Kostková, F. Halmo, V. Macho and L'. Jureček, *Chem. Prům.*, 1986, **36**, 128 (in Slovak); *Chem. Abstr.*, 1986, **105**, 62651h.
5 M. Górska and M. Gluzińska, *Chem. Anal. (Warsaw)*, 1973, **18**, 969 (in Polish); *Chem. Abstr.*, 1974, **80**, 33 631m.
6 M. Skarżyński, K. Gorczyńzska and E. Bednarek, *J. Mol. Struct.*, 1986, **143**, 541.
7 L. Malik, F. Halmo, N. Pronayová and T. Liptaj, *Petrochemia (Bratislava)*, 1986, **26**, 100 (in Slovak); *Chem. Abstr.*, 1987, **107**, 42 049f.
8 M. Skarżyński and W. Jakubowski, to be published.
9 M. Skarżyński, K. Gorczyńska and I. Leszczyńska, *Analyst*, 1999, **124**, 1823.
10 K. Gorczyńska, D. Ciecierska-Stokłosa and M. Skarżyński, unpublished results.
11 E. Zimnicka, unpublished results.