NEW POLYENOIC FATTY ACIDS IN NORWAY SPRUCE WOOD

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(Received 6 January 1979)

Key Word Index-Picea abies; Pinaceae; Norway spruce; polyenoic fatty acids; anteiso-fatty acids.

Saponification of the lipophilic extractives from the wood of Norway spruce, *Picea abies* (L.) Karst., yields a complex mixture of odd- and even-numbered straight-chain and *anteiso*-branched fatty acids with different degrees of unsaturation. The saturated fatty acids have been investigated in detail [1] and in further studies on the monoenoic acids in *P. abies* the occurrence of some unusual *anteiso*-monoenoic acids has been reported [2]. The major polyenoic fatty acids have also been identified [3].

The present paper reports the detection and characterization of five new polyenoic fatty acids, present in minor amounts in the wood of *Picea abies*: 16-methyloctadeca-5,9-dienoic (anteiso 5,9-19:2), 16-methyl-

octadeca-9,12-dienoic (anteiso 9,12-19:2), 16-methyloctadeca-5,9,12-trienoic (anteiso 5,9,12-19:3), eicosa-7,11,14-trienoic (7,11,14-20:3) and octadeca-5,9,12, 15-tetraenoic (5,9,12,15-18:4) acids.

Chain structures were determined by hydrogenation and the double bond positions were determined by GC-MS of the trimethylsilyloxy (TMSO) derivatives of the methyl esters obtained by OsO₄ hydroxylation of the double bonds and subsequent silylation.

Hydrogenation of the polyenoic methyl esters isolated on AgNO₃-TLC gave mainly methyl octadecanoate and methyl eicosanoate. Methyl 16-methyloctadecanoate (anteiso 19:0) was third in abundance whereas only trace amounts of methyl nonadecanoate

Table 1. Polyenoic fatty acids in Picea abies wood

Compound*	Percentage composition	ECL value BDS, 190°	TMSO derivative GC-MS 20 eV <i>m/e</i> (rel. int.)
anteiso 5,9-19:2	0.5	19.23	203 (A; 47), 371 (B-90; 52), 281 (B-180; 13), 345 (C-90; 100),
			255 (C-180; 33), 229 (D; 40)
anteiso 9,12-19:2	0.8	19.52	259 (A; 42), 405 (B; 10),
			315 (B-90; 97), 387 (C-90; 100), 297 (C-180; 12), 187 (D; 19)
anteiso 5,9,12-19:3	0.5	19.78	203 (A; 39), 457 (B-180; 18), 367 (B-360; 12), 345 (C-90; 62), 255 (C-180; 12), 315 (D-90; 100), 473 (E-180; 12), 383 (E-270; 32), 187 (F; 18)
5,9,12,15-18:4	1.2	19.89	203 (A; 46), 529 (B-270; 10), 439 (B-360; 11), 345 (C-90; 67), 255 (C-180; 13), 387 (D-180; 19), 297 (D-270; 15), 563 (E-90; 10), 473 (E-180; 11), 383 (E-270; 26), 349 (F; 10), 259 (F-90; 100), 601 (G-270; 10), 131 (H; 17)
7,11,14-20:3	1.0	21.19	231 (A; 32), 443 (B-180; 32), 353 (B-270; 36), 373 (C-90; 87), 283 (C-180; 18), 301 (D-90; 100), 591 (E-90; 10), 501 (E-180; 19), 411 (E-270; 33), 173 (F; 35)
5,9-18:2, 9,12-18:2 11,14-20:2, 5,9,12-18:3 9,12,15-18:3, 5,11,14-20:3	96.0		

^{*} Analysed as the methyl ester.

were detected. Equivalent chain length (ECL) values on GLC and mass spectra of reference samples verified the identifications.

The MS fragmentation pattern of the TMSO derivatives gives easily interpretable spectra with diagnostically important fragments and loss of trimethylsilanol from these, as exemplified below for a normal-chain diene derivative (1).

By analogy, additional characteristic fragments E, F (trienes) and E, F, G, H (tetraenes) are found in the spectra of more highly unsaturated derivatives (Table 1). The amount of polyenoic fatty acids in the investigated sample was 3.5 mg/g dry wood. Together the five new acids made up 4% of the fraction.

EXPERIMENTAL

A petrol (bp 40–60°) extract from fresh wood of *Picea abies* was saponified with 0.5 N KOH in EtOH– H_2O (9:1) at 70° for 4 hr. After addition of H_2O the unsaponifiables were extracted with petrol. The alkaline layer was neutralized with 0.5 N H_2SO_4 and the resin and fatty acids were extracted with several portions of Et_2O . The fatty acids were methylated by boiling in HCl–MeOH (1:20) for 2 min. H_2O was added and the fatty acid methyl esters and the free resin acids were extracted into Et_2O . The resin acids were removed by extraction of the Et_2O phase with 5% Na_2CO_3 . The GLC

distribution of the fatty acid methyl esters isolated in this way was identical with the composition of the methyl esters obtained by methylation of the saponification products using ${\rm CH_2N_2}$ and ${\rm BF_3\text{-}MeOH}$. The isolation of the polyenoic methyl esters on ${\rm AgNO_3\text{--}TLC}$ and the preparation of their TMSO derivatives were performed essentially as described previously [2]. Hydrogenation of the esters dissolved in iso-octane was achieved at room temp. by a slow stream of ${\rm H_2}$ for 1 hr and 10% Pd/C as catalyst.

The methyl esters of the polyenoic acids and their hydrogenation products were analysed by GC-MS using a $30\,\mathrm{m}\times0.3\,\mathrm{mm}$ id glass capillary column coated with 1,4-butanediol succinate (BDS). The column oven temp. was 190° . A $25\,\mathrm{m}\times0.3\,\mathrm{mm}$ id glass capillary column coated with SE-30 was used for the analysis of the TMSO derivatives; column temp. was $200\text{-}290^\circ$, $4^\circ/\mathrm{min}$. MS were recorded with a GC-MS instrument, model LKB-9000, operated at $70\,\mathrm{eV}$ (methyl esters) and $20\,\mathrm{eV}$ (TMSO derivatives).

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