was stirred at room temp for 4 hr, after the mixture was cooled to 0°, 34 g (32 ml, 0 3 mol) of 30% H_2O_2 was added The reaction mixture was stirred at 0° for 1 hr and extracted with Et_2O The Et_2O layer was separated, washed and dried The Et_2O was removed, and an oily liquid (7 3 g) was obtained which was a mixture of methyl pentyl disulfide and dipentyl disulfide Methyl pentyl disulfide was purified by prep GC and agreed in all its spectral properties with the natural compound

Pentyl hydrodisulfide was synthesized by oxidation of 1-pentanethiol (4 5 g, 0 05 mol) and Na_2S (3 9 g, 0 05 mol) with 34 g 30% H_2O_2 in 50 g 10% NaOH Pentyl hydrodisulfide was purified by prep GC and agreed in all its spectral properties with the natural compound

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Phytochemistry, Vol 22, No 1, pp 295–296, 1983
Printed in Great Britain

0031-9422/83/010295-02$03 00/0

n-ALKANES OF *HYPERICUM PERFORATUM*: A REVISION

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(*Received* 17 *May* 1982)

Key Word Index—*Hypericum perforatum*, Hypericaceae (Guttiferae), *n*-alkanes

Abstract—A study of the *n*-alkanes of *Hypericum perforatum* L revealed the presence of all members in the series C_{16}–C_{29} Contrary to previous reports the prevailing *n*-alkane was found to be nonacosane which was isolated in the pure state and identified on the basis of physical and spectral properties

INTRODUCTION

The presence of antibacterial substances in species of the genus *Hypericum* has been known for almost 40 years [1–3], extracts of *H perforatum* have been used clinically in Russia to treat infections [4], and in the U S A as a food preservative [3] Recently we reported on the relative stereochemistry [5] of the active principle which has been designated hyperforin [4, 6] As part of our study on the constituents of *H perforatum* which is commercially available as dried plant material from Scandinavian drugstores, we wish to report the results from an examination of the hydrocarbon fraction of the acetone extract

RESULTS AND DISCUSSION

GC/MS and co-chromatography with authentic alkanes revealed the presence of all *n*-alkanes in the series C_{16}–C_{29} Nonacosane ($C_{29}H_{60}$) prevailed and was obtained in virtually pure state (mp 63–64°) and identified beyond doubt on the basis of physical and spectral properties

Except for octacosane, none of these *n*-alkanes have previously been reported to be present in *H perforatum* Mathis and Ourisson claimed to have isolated a mixture of octacosane and triacontane ($C_{30}H_{62}$) judging from its mp, 63–64°, and mass spectrum [7] The former of these *n*-alkanes was present in our material in minute quantities (cf Table 1), while the latter was possibly present but in too small amounts to be identified with certainty Zellner and Porodko [8] reported on the hydrocarbons of *H perforatum* and suggested the presence of $C_{33}H_{68}$ and $C_{36}H_{74}$ on the basis of combustion analysis and MW determination according to Rast Because of the experimental errors associated with these methods, the fact that the mp (63°) of their $C_{33}H_{68}$-sample corresponds well with that of nonacosane, and due to the dominance of nonacosane in our plant material, we have reason to question the previously reported identifications of octacosane, triacontane and $C_{33}H_{68}$

Saturated straight and branched hydrocarbons of shorter chain have previously been reported to be present in the essential oil of *H perforatum* 2-methyloctane [9, 10],

Table 1 Distribution of *n*-alkanes in *Hypericum perforatum*

n-Alkane*	%
$C_{16}H_{34}$	2 0
$C_{17}H_{36}$	3 3
$C_{18}H_{38}$	5 7
$C_{19}H_{40}$	8 0
$C_{20}H_{42}$	6 3
$C_{21}H_{44}$	18 8
$C_{22}H_{46}$	3 7
$C_{23}H_{48}$	12 9
$C_{24}H_{50}$	1 6
$C_{25}H_{52}$	7 9
$C_{26}H_{54}$	0 3
$C_{27}H_{56}$	4 0
$C_{28}H_{58}$	0 2
$C_{29}H_{60}$	24 4

* Total wt of *n*-alkanes per kg dried material 1470 mg

n-nonane [9, 10], 3-methylnonane [10], *n*-decane [10], 2-methyldecane [10, 11], *n*-undecane [10, 11], *n*-tridecane [10] and 2-methyltridecane [10] Our GC analyses revealed minor peaks between those representing the *n*-alkanes which might be due to branched, saturated hydrocarbons However, they occurred in too small quantities to permit reliable identification

EXPERIMENTAL

Plant material Dried leaf material of *H perforatum* (*Herba hyperici*) was purchased from Norsk Medisinaldepot, Oslo A voucher specimen is deposited at the Department of Pharmacy, University of Oslo

Extraction and isolation Dried, powdered plant material (1 kg) was extracted with Me_2CO (8 l, 5 days) at room temp Portions (4 g) of the concd Me_2CO extract (25 g) were fractionated on a Si gel column (120 g) yielding non-polar fractions (747 mg each) on elution with $CHCl_3$ (400 ml) A partial separation of the shorter and longer chain hydrocarbons was achieved by re-chromatography of the non-polar material (4 6 g total), on a Si gel column (120 g), by elution with EtOH (500 ml) followed by *n*-hexane (500 ml) furnishing two major fractions (3335 mg and 1058 mg, respectively) These fractions were re-chromatographed on Si gel columns giving, on elution with *n*-hexane and *n*-hexane–$CHCl_3$ (9 1), sub-fractions consisting of satd hydrocarbons only, as judged from GC (2 5% OV-1, 180 cm × 1 9 mm silanized) and GC/MS The *n*-alkanes were, except in the case of nonacosane which was isolated in essentially pure state (see below), identified on the basis of their MS and by co-chromatography with authentic compounds, cf Table 1 One of the fractions crystallized and its main component (*ca* 90%, GC) was further purified via its urea complex yielding nonacosane, (358 mg), purity (GC) > 98%, mp 63–64° (*n*-hexane, lit [12] mp 64°), high resolution MS 408 4684 (calc for $C_{29}H_{60}$, 408 4695), ^{13}C NMR (15 MHz, $CDCl_3$) δ 14 1, 22 7, 29 7 and 32 0 (corresponding signals for authentic $C_{28}H_{58}$ δ 14 2, 22 8, 29 8 and 32 0)

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