Short Communications

Isolation of 1-Hexacosanol, Saturated Higher Fatty Acids, Oleic and Linoleic Acids from *Calamagrostis arundinaceae*

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As far as we know no chemical investigation has previously been undertaken concerning the common perennial grass, *Calamagrostis arundinaceae*. This paper reports on the examination of the lipid constituents of this species. The grass samples were collected in the month of September, only the flower-heads with seeds being used in the investigation. Extraction of the material with light petroleum yielded a coloured, viscous residue on evaporation of the solvent. By saponifying the residue, two fractions, A and B, were isolated as described in the experimental part. The results are of interest because they demonstrate that the main compound of the extractives is 1-hexacosanol (ceryl alcohol).

Identification of 1-hexacosanol. By recrystallization of fraction A (neutral part), a colourless, crystalline substance was obtained. NMR and IR spectra of this substance were consistent with an unbranched saturated aliphatic primary alcohol. HRMS showed the molecular ion at m/e 382.4171 (calc for $C_{26}H_{54}O$ 382.4175). A strong peak was seen at m/e 364 corresponding to the ion $C_{26}H_{53}^+$ ($M - H_2O$). The isolated substance was thus identical with 1-hexacosanol (ceryl alcohol). The identity of the C_{26} alcohol was further confirmed by elemental analyses.

Low and high resolution mass spectrometry also demonstrated the presence of small amounts of the higher fatty acids $C_{32}H_{64}O_2$ (dotriacontanoic acid), $C_{36}H_{72}O_2$ (triacontanoic acid), $C_{38}H_{76}O_2$ (nonacosanoic acid), and $C_{38}H_{76}O_2$ (octacosanoic acid). Long-chain saturated alcohols and acids often occur as constituents of plant waxes.¹ In the grass family ceryl alcohol has been found in the blades of *Dactylis glomerata* (cocksfoot) and *Lolium perenne*.²

Identification of unsaturated fatty acids. TLC of fraction B (a faintly yellow, viscous liquid) revealed several spots which turned yellow with phosphomolybdic acid in ethanol. Positive permanganate and tetranitromethane

tests showed the presence of unsaturated compounds. The mixture was dissolved in a sodium hydroxide solution and oxidized with permanganate by Lapworth's method.³ Recrystallization of the oxidized product afforded 9,10-dihydroxystearic acid and 9,10,12,13-tetrahydroxystearic acid (sativic acid) as shown by elemental analyses, IR, NMR, MS, and comparison with authentic samples. This provides strong evidence that fraction B was essentially a mixture of oleic and linoleic acids. These acids may be regarded as glyceride components of the investigated material.

Experimental. Elemental analyses and molecular determination were performed by Mikroanalytisches Laboratorium, Elbach, BRD. Chemical shifts in NMR spectra were recorded in δ -values. HRMS was performed by Shrader Analytical, Detroit, USA. The melting points are uncorrected.

TLC of the unsaturated fatty acids was carried out on precoated plates with cellulose as absorbent. Toluene-acetic acid (85 + 15) was used as solvent, and spots were rendered visible with phosphomolybdic acid in ethanol.

Extraction and isolation of the constituents. Dried and ground grass (773 g) was extracted in a Soxhlet apparatus with light petroleum (60–80 °C) for 5 h. The solution was evaporated at reduced pressure and the residue refluxed in 450 ml of a 5 % solution of potassium hydroxide in methanol. After dilution with water the insoluble constituent was filtered off and treated with dilute HCl. Recrystallization first from ethanol and then from acetic acid gave fraction A, yield 380 mg, m.p. 72.4 °C. Anal. $C_{26}H_{53}OH$: C, H, O. 1H NMR (60 MHz, $CDCl_3$): δ 0.88 (aliphatic C–CH₃), 1.27 (straight chain CH₂ groups), 1.60 (CH₂CH₂OH), 2.09 (OH), 3.63 (CH₂OH). IR (Nujol, Hostafion, KBr): 3250 (polym. ass. of OH groups), 2960 (asym. CH stretch vibr.), 1055 (CO stretch vibr. of primary alcohol), 720 cm^{-1} (straight chain CH₂ groups, singlet).

The aqueous alkaline solution after acidification was then extracted with ethyl ether. On evaporation the ethereal solution left a yellowish oily liquid, fraction B, which solidified on cooling. Oxidation of the unsaturated fatty acids in fraction B was carried out in an alkaline solution with 0.2 % aqueous potassium permanganate. After 10 min the solution was acidified with HCl, and NaHSO₃ was added until the excess permanganate and manganese(IV) oxide had been converted to manga-

nese(II) sulfate. The oxidized components were removed by filtration. Separation of the components was effected by concentrating the solution in ethanol to about 125 ml. On cooling slowly to 0°C a crystalline *Substance B1* separated out. The substance was recrystallized from acetic acid, m.p. 158°C. ^1H NMR (60 MHz, $\text{DMSO}-d_6$): δ 0.88 (CH_3), 1.30 (CH_2), 2.20 ($\text{CH}_2\text{CO}_2\text{H}$), 3.30 (CHOH). MS of B1 showed no molecular ion. Prominent peaks were observed at m/e 113, 155, 157, 173, and 229 corresponding to the fragments outlined in a previous communication.⁴ IR comparison with authentic 9,10,12,13-tetrahydroxystearic acid (sativic acid) demonstrated a complete agreement. Found: C 62.58; H 10.25; O 27.24. Calc. for $\text{C}_{18}\text{H}_{36}\text{O}_6$: C 62.04; H 10.41; O 27.55.

On evaporation of the filtrate above, a crystalline mass remained. This was purified by recrystallization from acetic acid and chloroform. A *Substance B2*, yield 170 mg, m.p. 125°C, snow-white crystals, was finally obtained. Anal. $\text{C}_{18}\text{H}_{36}\text{O}_4$: C, H, O. MW (osmometric in pyridine): Found 308, calc. 316.5. IR(KBr) and ^1H NMR (in $\text{DMSO}-d_6$) spectra agreed completely with those of an authentic sample of 9,10-dihydroxystearic acid.

In the mass spectrum, dominant and characteristic peaks were found. HrMS (m/e): 281 ($\text{M}-\text{H}_2\text{O}-\text{OH}$), 280 ($\text{M}-2\text{H}_2\text{O}$), 229 ($\text{M}-\text{C}_6\text{H}_{13}-\text{OH}$), 185 ($\text{HO}^+=\text{CH}-\text{CH}=\text{CH}-(\text{CH}_2)_6-\text{CO}_2\text{H}$), 175 ($\text{HO}-\text{CH}_2-(\text{CH}_2)_7-\text{C}(\text{OH})=^+\text{OH}$) and 173 ($\text{HO}^+=\text{CH}-(\text{CH}_2)_7-\text{CO}_2\text{H}$). The base peak at m/e 155 corresponded to the fragment $\text{HO}^+=\text{CH}-(\text{CH}_2)_6-\text{CH}=\text{C}=\text{O}$.

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Stable α -Chloro- β -oxosulfenyl Chlorides: a Novel Class of Compounds Formed from Ketones and Thionyl Chloride

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Reaction of monosubstituted acetic acids *1a* or acetonitriles *1b* with thionyl chloride in the presence of a tertiary amine, or $\text{Et}_3\text{N}/\text{HCl}$, respectively, produces α -chlorosulfenyl chlorides *2a* and *2b*.¹⁻⁷ By analogy, α -chloro- β -oxo-

sulfenyl chlorides *3* have been invoked as transient intermediates in reactions between ketones and thionyl chloride leading to 3-thietanones and benzo[*b*]thiophenes.^{8,9} The first stable representatives of this class of organic sulfur compounds are described in the following.

When the hindered ketones *5a* and *5b* are allowed to react with thionyl chloride, without any added catalyst, two products are formed, to which the structures *6a* and *6b* are assigned on the basis of elemental analysis and spectroscopic properties, see Experimental.

Though various pathways to the formation of *6a* and *6b* can be envisioned,⁸ the evidence is insufficient to warrant further comments at this stage.

Experimental. ^1H NMR were recorded on a Varian 360 instrument, and ^{13}C NMR on a Bruker WH-90 at 22.63 MHz with broad band noise ^1H -decoupling. Long relaxation times are indicated by an *a*. The mass spectrum of *6a* was recorded on a Perkin-Elmer 270 instrument; exact measurement was performed on an AEI MS 3074 instrument. The spectrum of *6b* was recorded on a DuPont 21-492 instru-