Leaf and stem (50 g): Isolation by standard procedures[2] gave agnuside (1 %) and aucubin (0·4 %), identified by comparison of the IR spectra with those of authentic substances and by co-chromatography [PC: *n*-BuOH–MeOH–H_2O (4:1:5, upper); isopentanol–HOAc–H_2O–*n*-hexane (3:3:3:1), upper. TLC: CH_2Cl_2–MeOH–H_2O (40:10:1) on silica gel]. Ecdysones could not be detected.

Plant. Vitex rehmanni Gürke. *Source.* South Africa.

Leaf and stem: Air dried plant material (200 g) was worked up using standard procedures[2] to give 200 mg aucubin (0·1 %) and a mixture of agnuside and ecdysterone. The mixture was separated by column chromatography on polyamide. Elution with H_2O afforded 1·9 g agnuside (1 %) and 10 mg ecdysterone (0·005 %). Ecdysterone was identified by comparison of IR and MS with those of an authentic sample. Identification of iridoids see above.

Plant. Vitex sereti De Wild. *Source.* Congo.

Leaf and stem (95 g): Agnuside (0·05 %), ecdysterone (0·02 %). Isolation and identification see above.

Voucher specimens: Institut für Pharmakognosie der Freien Universität Berlin.

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MONOCOTYLEDONAE

GRAMINEAE

HYDROXY-HENTRIACONTANEDIONES FROM *AVENA SATIVA*

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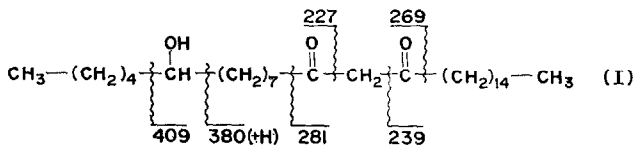
Key Word Index—*Avena sativa*; Gramineae; 5-, 6- and 7-hydroxy-*n*-hentriacontane-14,16-dione.

Plant. Avena sativa L. cv. Seger I de Svalöv; caryopses. *Source.* Allmänna Svenska Utsädes A.-B., Svalöv, Sweden. *Previous work.* The 25-[1,2] and the 8- and 9-[3–5] isomers were cited from other cereals.

[1] A. P. TULLOCH and L. L. HOFFMAN, *Phytochem.* **10,** 871 (1971).
[2] K. BUFFEL, unpublished results.
[3] A. P. TULLOCH and R. O. WEENINK, *Chem. Commun.* **8,** 225 (1966).
[4] A. P. TULLOCH and R. O. WEENINK, *Can. J. Chem.* **47,** 3119 (1969).
[5] L. L. JACKSON, *Phytochem.* **10,** 487 (1971).

Present work. Caryopses were extracted with light petroleum (30–45°). The waxy residue was adsorbed to basic Al_2O_3 and eluted with light petroleum (30–45°). TLC of this residue on silica gel G; benzene; detection with Fast Blue B salt (Merck); R_f 0·11. Elution of this zone with Et_2O. Recrystallization from Et_2O gave white thin needles.

IR bands (KBr) ν_{max} 3340, 2900, 2840, 1715, 1640 (β-diketone), 1465, 1410, some small peaks between 1300 and 1170, 1140, 1100, 1025, 790, 775, 730 and 720 cm^{-1}. UV band (Et_2O) λ_{max} 274 nm. MS showed a molecular ion mass peak of 480 *m/e*. Previous work[2] in this laboratory led to the isolation of the 25-OH–C_{31}-14,16-dione from barley germ roots. This substance (MW = 480) was identified by high resolution MS, which gave the molecular formula $C_{31}H_{60}O_3$. A characteristic IR band at 1640 cm^{-1}, the deep yellow colour with Fast Blue B salt, and the MS fragmentation pattern revealed a straight C_{31}-chain with two C–O functions at position 14 and 16, and an OH at position 25.



(I)

As our dionol from oats had the same molecular ion peak and exactly the same colour reaction with Fast Blue B salt, we believed it to be an isomer (or mixture of isomers) of the barley dionol, which afterwards was found in complete accordance with the fragment-ions spectrum. Fragmentation on both sides of the secondary alcoholgroup gave peaks at 423 and 394 *m/e* for the 5-, at 409 and 380 *m/e* for the 6-, and at 395 and 366 *m/e* for the 7-isomer. Other major ions were observed at 281, 227, 239 and 269 *m/e*, displaying the fragmentation shown on the structure (I). McLafferty rearrangement accounted for the peaks at 296 and 284 *m/e*. M^+-H_2O peaks at 444 and 462 *m/e*. The withdrawal of water from fragmentions gave peaks at 362, 348, 376, 278, 251, 266, 248, 209 and 191 *m/e*. According to the relative abundance of the peaks at 395, 409 and 423 *m/e* this mixture of isomers consisted of 20% 5-, 50% 6- and 30% 7-OH-*n*-C_{31}-14,16-dione.

Comment. From this and other investigations[3–5] it now appears that the introduction of the OH-group is not positionally specific in the C_{13}-part of the molecule, whereas it is introduced in the C_{15}-side[1,2] precisely on the C_{25}. This has probably a biogenetic importance. In any case the biogenesis of these 3 compounds can not be explained by the addition of water to one double bond nor by the opening of an epoxide ring, as suggested earlier.[1]