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A Note on the Constitution of the Diterpene $C_{20}H_{28}O_3$ from *Solidago canadensis* L.

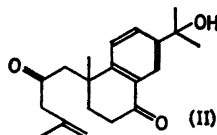
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In 1947 Houston and Burrell¹ described a diterpene $C_{20}H_{28}O_3$ (I) from the roots of *Solidago canadensis* L. The m.p. of the primary crystals was 89–90°C, changed to 131–132°C on recrystallisation. The diterpene was devoid of carbonyl functions and did not react with metallic sodium in benzene.

During investigations of members of Compositae for acetylenes *S. canadensis* also has been investigated. The plant was seemingly devoid of acetylenes, but the diterpene described by Houston and Burrell was isolated in good yields and was studied by spectroscopic methods and some preliminary chemical reactions also were carried out.

In a recent note Gerlach² reports investigations on the same diterpene (I) and proposes the constitutional formula (II).



It is remarkable that formula (II) gives $C_{20}H_{28}O_3$, $M = 314$, whereas Gerlach's own analysis agrees with that given by Houston and Burrell, $C_{20}H_{28}O_3$, $M = 316$, and this is also found by Gerlach's mass spectroscopic measurement. We have obtained the same molecular peak 316 and so the $C_{20}H_{28}O_3$ formula for (I) is fully confirmed.

Although our spectroscopical data mostly agree well with those of Gerlach, our interpretation does not allow any of the elements contained in (II).

The UV-spectrum of (I) has one sharp band at 222 $m\mu$ (Gerlach gives 224 $m\mu$) quite incompatible with formula (II), which would be expected to show strong absorption in the 295 $m\mu$ and 250 $m\mu$ ranges (expected ϵ about 2000 and 14 000).

Our NMR-spectrum, cf. Fig. 1, agrees as to position of the bands to the values given

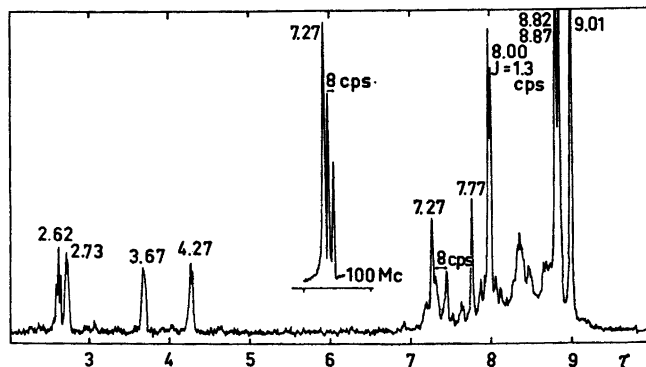


Fig. 1. NMR-spectrum of *Solidago* diterpene $C_{20}H_{28}O_3$ in $CDCl_3$; 60 Mc, Varian A 60; 100 Mc, Varian HA 100.

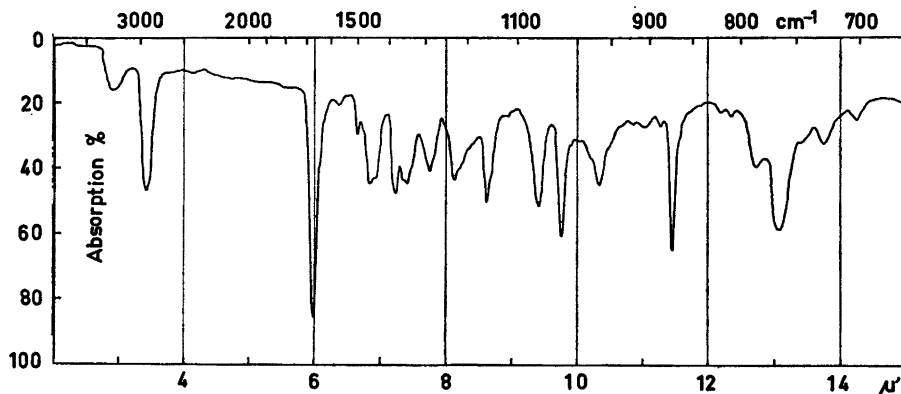


Fig. 2. Infrared spectrum of *Solidago* diterpene, $C_{20}H_{38}O_3$, in $CHCl_3$ (Perkin Elmer M 21). (12–15 μ range KBr-disk).

by Gerlach. By comparison with literature values for simple 3-substituted furans³ and terpenoids of this type⁴ the bands with $\tau = 2.62$, 2.73, and 3.67 definitely indicate two α -protons and one β -proton on a furan ring. 3-Alkyl-furans usually absorb in the region 210–220 $m\mu$. The combined UV and NMR data, therefore, are taken to indicate the presence in the molecule of a 3-substituted furan ring. This is further confirmed by sharp bands in the infrared spectrum (*cf.* Fig. 2) at 1567, 1502, 873, and 763 cm^{-1} ; *cf.* Ref. 5.

(I) reacts smoothly with maleic anhydride to an adduct where the furan bands

in the infrared have disappeared. As to be expected the adduct is reversibly split into the starting materials by heating in a vacuum.

The diterpene further gives a positive Ehrlich test for furans and an orange-red colour in acetic acid by addition of a few drops of sulphuric acid according to Quilico *et al.*⁶ Finally the presence of the furan ring is confirmed by the mass spectrum, *cf.* Fig. 3. The peaks at 81 (C_5H_5O) and 95 are typical of diterpenes with a 3-substituted furan residue.^{7,8}

As reported by Gerlach, M-18 (= 298) is a definite peak in the mass spectrum, as

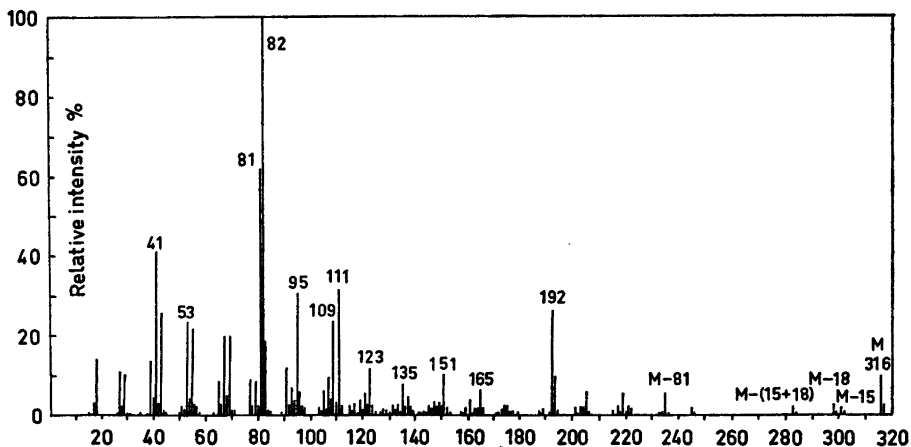


Fig. 3. Mass spectrum of *Solidago* diterpene, $C_{20}H_{38}O_3$, Hitachi-Perkin-Elmer by Dr. J. Seibl, E.T.H., Zürich.

can be seen from Fig. 3. The intensity of M is four times that of M-18. Most hydroxyl containing diterpenes either lack the mass peak M or have $M \ll M-18$. A recent communication by Enzell and Ryhage⁷ contains one example, marrubiin, with $M > M-18$ (however, compare Reed and Reid⁸ who, apparently, observed neither M nor M-18 in the mass spectrum of marrubiin).

The IR- and NMR-spectra indicate that (I) could contain one hydroxyl group. However, under standard conditions (I) does not form a trimethylsilyl ether, indicating the hydroxyl group to be sterically hindered. (I) very easily splits off water by treatment with small amounts of acid catalysts. The reaction is very complex, and probably involves the third oxygen function.

In agreement with Houston and Burrell no reactions for carbonyl groups were obtained. The UV absorption at $222 \text{ m}\mu$ does not allow the very strong band at 1667 cm^{-1} to be interpreted as belonging to a conjugated carbonyl group. More reasonably it could be taken as a vinyl ether band ($\text{HC}=\text{C}-\text{O}-$) which according to Rosenkrantz and Gut⁹ is usually found close to 6μ and always very intense. (Our preparation of (I) does not show any IR band at 1780 cm^{-1} (weak) as given by Gerlach; otherwise the agreement is complete.)

Reduction of (I) with LiAlH_4 gave a very complex mixture, one of the main components being a non-conjugated ketone (band at 1704 cm^{-1}) with loss of the 1667 band but retention of all furan bands. One of the few elements which by LiAlH_4 reduction gives rise to a ketone is just vinyl ethers; cf. Ref. 10.

In analogy with the splitting pattern of known diterpenes the mass spectrum — particularly the metastable peaks at 117 and 35 — are interpreted to indicate ($316 \rightarrow 192 + 124$, $192 \rightarrow 82 + 110$) that (I) does contain a normal ring A without oxygen substituents.

Further experiments to elucidate the structure of the element $\text{C}_7\text{H}_9\text{O}_2$ uniting the furan ring with ring A are in progress.

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Correction to "The Structure of (+)- ϵ -Muurolene (" ϵ -Cadinene")"

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The muurolene dihydrochloride described in a previous communication* was incorrectly referred to as being the (+)-form. The rotation of the compound was actually -13.2° and not $+13.2^\circ$.

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