Stereochemistry of Clerodanes. *X*-Ray Structure of a Key Diterpenoid from *Solidago Arguta* Ait

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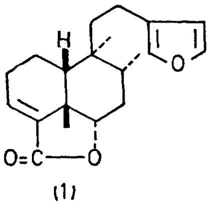
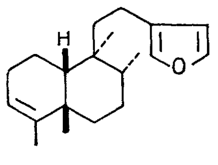
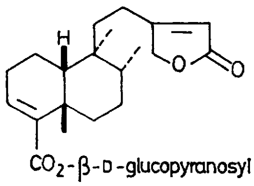
Summary *X*-Ray structural studies of the diterpenoid (**1**) from *Solidago arguta* have confirmed the relative stereochemistries assigned to (**1**) and a large group of related compounds including marrubiaside (**3**), (—)- hardwickiic acid (**4**), and kolavenic acid (**5**).

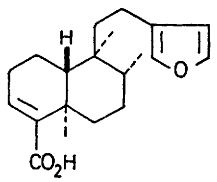
Recently we presented[1] evidence for a *cis*-clerodane skeleton in several diterpenoids from *Solidago arguta* including (**1**) and (**2**) and suggested that several other compounds of natural provenance are also based on this skeleton. Since then we have effected[2] a correlation between marrubiaside (**3**)[3] and (**2**), which in addition has been prepared[4] from a new diterpenoid isolated from a member of the Scrophulariaceae. Our stereochemical assignments[1] were based on a correlation of (**2**) with the *trans*-clerodane, (—)-hardwickiic acid (**4**),[5] which in turn has been interrelated with a large number[6] of natural products including kolavenic acid (**5**). Although the chemical and spectral evidence for the *trans*-clerodane skeleton in (**4**) and (**5**) appeared reasonably sound it seemed desirable, in view of the very large number of diterpenoids involved, to obtain an *X*-ray structure for one of the compounds discussed above.

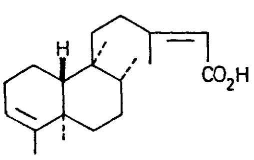

(1)


(2)



(3)


(4)


(5)

We attempted to prepare suitable heavy-atom derivatives of several of them in order to facilitate structure solution and to establish the absolute configuration by anomalous dispersion methods. However, no suitable crystalline material was obtained and accordingly we examined the non-heavy atom derivative (**1**) in order to establish the relative stereochemistry.

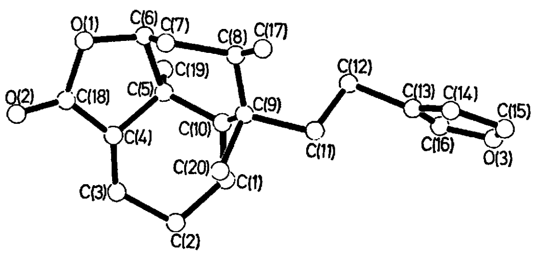


Figure. The structure of (**1**) viewed along *b*.

Crystals of (**1**) are monoclinic, space group $P2_1$ with 2 molecules of $C_{20}H_{26}O_3$ in a unit cell of dimensions $a = 7{\cdot}908$, $b = 11{\cdot}225$, $c = 14{\cdot}445$ Å, $\beta = 137{\cdot}16°$. The structure was solved by direct methods using 831 observed reflexions measured on a diffractometer. After initial full-matrix least-squares refinement $R = 0{\cdot}090$. The refinement is continuing. A view of the molecule showing the stereochemistry at the various centres is given in the Figure.

Since the optical evidence[5,6], for the absolute configuration at C-5 and C-10 in (—)-hardwickiic acid (**4**) appears totally acceptable, the C-8, C-9, C-10, C-5 stereochemistry of the series of *trans*- and *cis*-clerodanes which have been correlated with (**4**) and (**2**) respectively can now be drawn with confidence [as in (**2**) and (**4**)].

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