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ACID-CATALYZED REARRANGEMENT OF ABIESLACTONE

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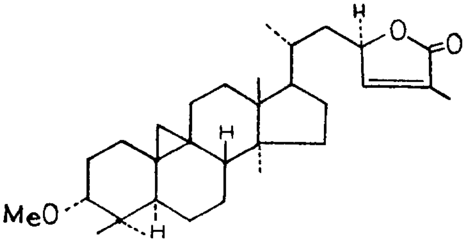
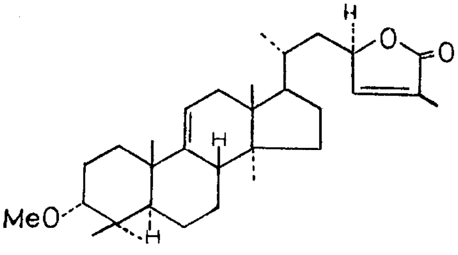
Very recent communication[1] has established the structure of cyclograndisolide (I) by the X-ray crystallographic analysis of its heavy atom derivative and has shown that the product obtained by treatment of this compound with hydrogen chloride in chloroform is not identical with abieslactone for which we had advanced structure (II),[2] but is indistinguishable from the compound which was isolated by treatment of abieslactone with hydrogen chloride. This finding prompted us to remind of an earlier report by Takahashi[3] that while abieslactone gave a compound, m.p. 213-215° on treatment of it with hydrochloric acid in alcohol, it yielded a higher melting product, m.p. 224-227° with sulfuric acid in alcohol. We have confirmed this finding and found that boron trifluoride converts abieslactone into the same compound as that with sulfuric acid. The lower melting compound thus obtained was assumed to be identical with grandisolide,[1] since it was also obtained from abieslactone under the same condition as employed by the Canadian authors. Careful examination of the NMR spectrum of grandisolide revealed that its homogeneity was questionable. Integrated intensity of one of the olefinic protons (τ 4.66-5.28) overlapping with the proton on the carbon bearing the lactone oxygen on the side chain is ca. 1.7H and not 2H as expected from structure (II). On the other hand, the higher melting compound, m.p. 224-227°, exhibited signals in the same region, integration of which corresponded to 2H.

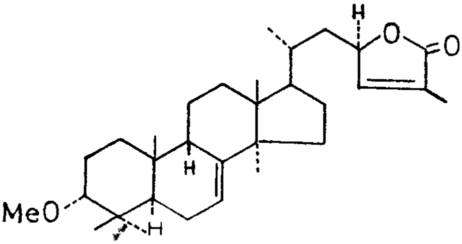
Further evidence for this inference was provided by the CD curve of these two transformation products. The Cotton effect due to $\pi \rightarrow \pi^*$ transition of the olefinic



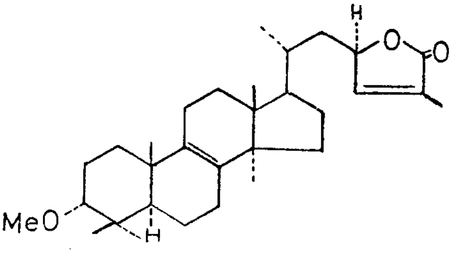
(I)



(II)



(III)



(IV)

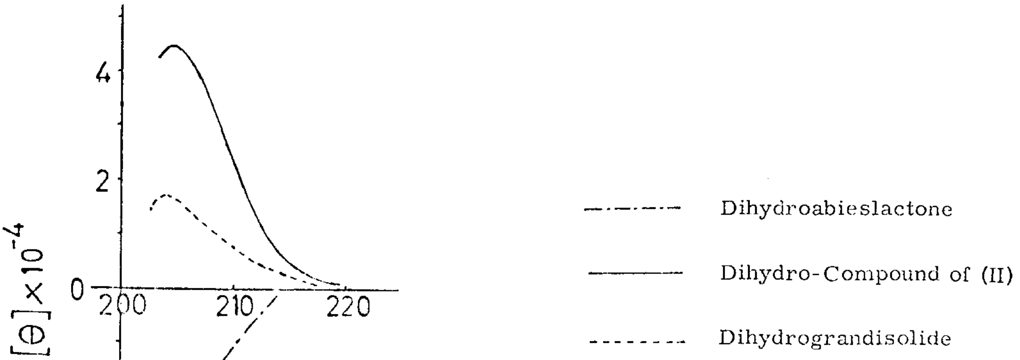


Fig. 1. CD curves of dihydro derivatives of abieslactone, grandisolide and compound (II).

linkage both in dihydro derivative, m.p. 239-240°, of the higher melting transformation product and in dihydrograndisolide, m.p. 226-228° exhibited a positive maximum at 204 nm in good agreement with the data of androst-9, (11)-ene series[4]. However the amplitude of the former compound was far larger than that of the latter [Fig. 1] indicating that dihydrograndisolide is contaminated with the compound (IV) containing a double bond at 8, 9-position, since the CD curve of the compound containing the double bond at this position is reported to show a weak peak in the same region.

In contrast, the CD curve of dihydroabieslactone showed a strong negative sign which is not in accord with the structure (II)as proposed previously,[2] but is indicative of a structure with a double bond at 7, 8-position. Considering the important contribution[5] of the α-axial proton to the rotatory power of a double bond, no negative maximum at 205 nm suggests C_9-βH configuration with ring C of a boat form. These findings are in good agreement with structure (III) which was elegantly elucidated by the X-ray crystallographic analysis of abieslactone by Professor Kutney and his associates.[6, 7]

It is probable that the shift of the double bond at 7, 8-position in abieslactone to 9, 11-position by treatment with sulfuric acid or boron trifluoride is in a concerted manner and in fact, treatment of abieslactone with di-deuteriosulfuric acid in deuteriomethanol furnishied the monodeuterio-derivative of the compound (II) (M^+ 469). On the other hand, treatment of abieslactone with hydrochloric acid gave rise to at least in part a carbonium ion at position 8 or 9 which would be stabilized by forming a double bond either at 9, 11- or 8, 9-position, since treatment of abieslactone with deuteriochloride in chloroform afforded dideuterio-compound(s) (M^+ 470) along with the monodeuterio-compound (M^+ 469).

It is obvious that the strain caused by the unusual βH-configuration at C_9 in abieslactone facilitates greatly the rearrangement of the double bond at 7, 8-position by mineral acids.[8, 9]

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(7) We are grateful to Professor Kutney for letting us have a copy of their manuscript prior to publication.

(8) We are grateful to Dr. J. W. Rowe, Forest Products Laboratory, Forest Service, United States Department of Agriculture, Madison, Wisconsin, for valuable discussion.

(9) In a recent report, E.E. van Tamelen and J.W. Murphy, J. Amer. Chem. Soc., 92, 7204 (1970), indicate isomerization of a $C_9\beta$-7,8-unsaturated lanostene derivative to a mixture of the 9α-7,8-ene and 8,9-ene compounds.