Tetrahedron Letters No.34, pp. 2323-2327, 1964. Pergamon Press Ltd.
Printed in Great Britain.

ARUNDOIN - A NATURALLY-OCCURRING D:C-FRIEDO-OLEANA-9(11)-ENE

G. Eglinton and R. J. Hamilton
Department of Chemistry, The University, Glasgow, W.2,
Scotland.
M. Martin-Smith, S. J. Smith and G. Subramanian
Department of Pharmacy, The Royal College
of Science and Technology, Glasgow, C.1.

(Received 3 July 1964)

An earlier examination[1] of the leaf surface wax and of the light petroleum extractives of the whole dried leaves of the New Zealand toë-toë grass (Arundo conspicua) revealed the presence of ethers, which have now been characterised as triterpenoid monomethyl ethers. The ether, $C_{31}H_{52}O$, m.p. 248-250°, present in minor amount was found to be β-amyrin methyl ether (isosawamilletin[2]) on comparison with an authentic sample (i.r., g.ℓ.c. and mixed m.p.), whilst the more abundant isomeric compound, $C_{31}H_{52}O$ m.p. 235-237° and 271-273° (dimorphic forms), $[\alpha]_D = -9°(c = 1.7$ in $CHCl_3)$, which has been assigned the name arundoin, has been shown to be the methyl ether of 3β-hydroxy-D:C-*friedo*-oleana-9(11)-ene (I).*

The occurrence in grasses of triterpenoid methyl ethers lacking other

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[1] G. Eglinton, R. J. Hamilton and M. Martin-Smith, Phytochemistry, 1, 137 (1962).

[2] S. Abe and T. Obara, Nippon Kagaku Zasshi, 80, 1487 (1959).

* Nomenclature after S. Allard and G. Ourisson, Tetrahedron, 1, 277 (1957).

oxygen functions is well authenticated[2-4] but arundoin would appear unique in being the first naturally-occurring D:C-*friedo*-oleana-9(11)-ene having normal stereochemistry at C-13 and C-14[5] to be reported.

The mass spectrum of arundoin showed the molecular weight to be 440 and indicated that it was a pentacyclic triterpene since there was no peak corresponding to loss of side chain[6,7]. Prominent peaks at $\overline{\text{P-15}}$ and $\overline{\text{P-15-32}}$ indicated elimination of a methyl group followed by elimination of methanol from the ether system, whilst strong peaks at m/e 273 and m/e 241, also related by loss of methanol and hence arising from the fragment containing the ether function, were in agreement with the cracking pattern to be expected of a $\Delta^{9(11)}$ triterpenoid bearing a methoxyl group at C-3[5,8,9].

The nuclear magnetic resonance spectrum of arundoin was also in agreement with the presence of a 3-methoxyl function as evidenced by absorption of intensity 4 protons at 6.62 τ - the high field absorption of the -O-CH< proton being attributable to shielding by the gem dimethyl groups on C-4. A multiplet at 4.65 τ, intensity one proton, showed the trisubstituted nature of the double bond, the presence of which was confirmed by the i.r. and u.v. spectra of arundoin.

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[3] S. Abe, *Bull. Chem. Soc., Japan*, **33**, 271 (1960).

[4] S. Abe, *Nippon Kagaku Zasshi*, **80**, 1491 (1959); **82**, 1057 (1961).

[5] *Cf*. H. Vorbrüggen, S. C. Pakrashi and C. Djerassi, *Liebigs Annalen*, **668**, 57 (1963).

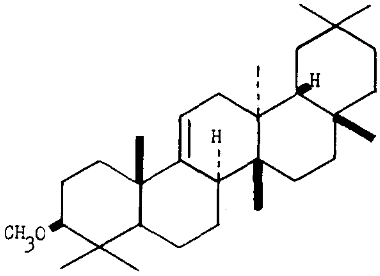
[6] R. I. Reed and P. De Mayo, *Chem. & Ind.*, 1481 (1956).

[7] H. Budzikiewicz and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1430 (1962).

[8] H. Budzikiewicz, J. M. Wilson and C. Djerassi, *J. Amer. Chem. Soc.*, **85**, 3688 (1963).

[9] K. Nakanishi, Y. Y. Lin, H. Kakisawa, H. Y. Hsu and H. C. Hsiu, *Tetrahedron Letters*, No. 22, 1451 (1963).

Accordingly arundoin was converted into the corresponding 7,9(11)-diene in order that comparison could be made with the 7,9(11)-dienes derived from the methyl ethers of arborinol[5], isoarborinol[5], multiflorenol[10] and bauerenol[10,11]. In the event the 7,9(11)-diene derived from arundoin proved identical (i.r., u.v. mixed m.p.) with that obtained from the methyl ether (II) of multiflorenol. The diene can therefore be assigned structure III, and the structure of arundoin is confirmed as I in view of the non-identity of arundoin with multiflorenol methyl ether. The assignment of α-configuration to the hydrogen at C-8 in I is based on biogenetic considerations since it would appear that this hydrogen atom has migrated from C-9 as in the biogenesis of glutinone and friedelin[12] and that the formation of arundoin involves stoppage of the backbone rearrangement suffered by the fundamental pentacyclic oleanane bridged carbonium ion[12] at a stage between that giving rise to multiflorenol on



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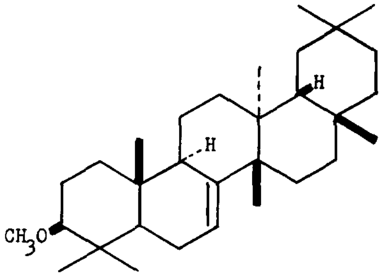

II

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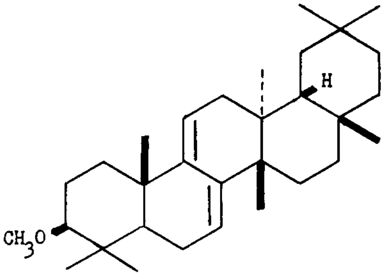
[10] P. Sengupta and H. N. Khastgir, *Tetrahedron*, **19**, 123 (1963).

[11] T. N. Lahey and M. V. Leeding, *Proc. Chem. Soc.*, 342 (1958).

[12] L. Ruzicka, *Proc. Chem. Soc.*, 341 (1959).

the one hand and that giving rise to glutinone on the other. The occurrence in nature of germanicol, δ-amyrin, β-amyrin, taraxerol, multiflorenol, arundoin, glutinone and friedelin moreover suggests a highly selective control of the degree to which this backbone rearrangement is permitted to proceed in different plant species and it remains to be seen whether derivatives of the three remaining possible types, viz., D:C-friedo-oleana-8-ene, D:B-friedo-oleana-1(10)-ene and D:B-friedo-oleana-5(10)-ene will be found to be of natural occurrence.



III

Like arborinol[5] which has the opposite configurations at C-8, C-13, C-14 (and so corresponds to 24,25-dihydroparkeyl acetate[13-15]), arundoin failed to react with selenium dioxide or to suffer double bond rearrangement under the influence of hydrogen chloride in chloroform.

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[13] D. S. Irvine, J. A. Henry and F. S. Spring, J. Chem. Soc., 1316 (1955).

[14] H. R. Bentley, J. A. Henry, D. S. Irvine and F. S. Spring, J. Chem. Soc., 3673 (1953).

[15] W. Lawrie. Ph.D. Dissertation, University of Glasgow, 1957.

In view of the failure to react with selenium dioxide arundoin was converted into the diene III by a sequence analogous to that employed in the arborinol series[5], involving epoxidation with trifluoroperacetic acid, acid catalysed elimination from the epoxide and chromatographic purification of the product. The ultraviolet spectrum of III with λ max 232, 239, 247.5 mμ; ϵ 16,100, 16,900, 9,500 was in agreement with the ultraviolet spectra of other triterpene 7,9(11)-dienes having 13α- and 14β-methyl groups[10,11,16] which differ from those of triterpene 7,9(11)-dienes having methyl groups in the 13β and 14α configurations[5,16].

In the present work etherification of all 3-hydroxy compounds was accomplished under nitrogen by means of methyl iodide in dry benzene employing potassium sand as base.

Acknowledgements: The authors gratefully acknowledge gifts of miliacin, isomiliacin, sawamilletin and isosawamilletin by Dr. S. Abe of the Yamazaki Works, Japan and of other triterpenes by Drs. C. J. W. Brooks and J. McLean. They also wish to express their gratitude to Drs. J. McLean, W. Lawrie and J. M. Wilson for their interest and helpful suggestions. They are indebted to Drs. R. I. Reed and W. K. Reid for mass spectra, to Drs. A. L. Porte and P. Bladon for nuclear magnetic resonance spectra, to Mrs. F. Lawrie for infra red spectra, to Mr. J. M. L. Cameron for microanalyses and to Miss Irene Wilson for extraction of arundoin. One of us (M.M.-S.) gratefully acknowledges generous financial support from the Royal Society and the Pharmaceutical Society of Great Britain in connection with the collection of the plant material which was dried through the courtesy of Dr. A. T. Johns, Plant Chemistry Division, Grasslands Research, D.S.I.R. (New Zealand). Another (R.J.H.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant and a third (S.J.S.) acknowledges tenure of a Todd Research Trust Fund Grant.

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[16] M. C. Dawson, T. G. Halsall and R. E. H. Swayne, J. Chem. Soc., 590 (1953).